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Adsorption of cucurbit[6]uril at an electrode/solution interface

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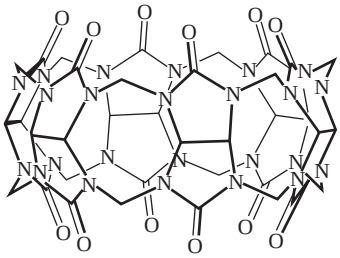
The behavior of cucurbit[6]uril at the electrode/solution interface was examined and quantified in the wide ranges of electrode potentials and adsorbate concentrations.



cucurbit[6]uril

Cucurbit[6]uril is the first synthesized member of the homologous family of new macrocyclic cavitands.[1] These pumpkin-shaped macrocycles consist of *n* repeating glycoluril units connected by methylene bridges. The bottom and the top of these molecules represent two carbonylated rims that serve as portals. Cucurbiturils with *n* from 5 to 10 were synthesized. These macrocyclic ligands are of interest due to their exceptional recognition properties in aqueous solutions: cucurbiturils can encapsulate organic molecules or ions in their hydrophobic inner cavity and simultaneously bind metal cations due to their interaction with carbonyl groups at the portals. Macrocyclic cavitands CB[*n*] offer promise for application in biochemistry, medicine and nanotechnology.[2] They can also be used as building blocks for the synthesis of supramolecular compounds and hybrid organo-inorganic materials on their basis.[3]

The portals of these ligands can interact with the surfaces of metals (gold, silver, and palladium) and oxides (titanium dioxide).[4,5] However, the properties of the adsorption layers of cucurbiturils at interfaces are poorly understood. Previously, we studied the properties of cucurbit[5]uril (CB5) at an electrode/solution interface.[6] The aim of this work was to study the adsorption of cucurbit[6]uril (CB6) at the Hg electrode/0.1 M Na_2SO_4 solution interface. Cucurbit[6]uril was synthesized in 1905,[1] but its structure was elucidated only in 1981.[7] The outer diameter and the height of the CB6 molecule are 1.44 and 0.91 nm, respectively. The inner cavity has a diameter of 0.58 nm and a volume of 0.164 nm^3. With the Na^+ cation, CB6 forms a 1 : 1 complex with the stability constant lg K_s = 3.49.[8,†]

The differential capacity *vs.* potential (*C vs. E*) curves of a mercury electrode were measured in 0.1 M Na_2SO_4 aqueous solutions containing CB6 in concentrations from 2.5×10^{-4} to 10^{-5} mol dm^{-3} (Figure 1). It is evident that the adsorption behavior of CB6 is similar to that for CB5: the unusually wide potential range (2 V), in which *C* remains lower than that in the background solution, *i.e.*, the adsorption of this compound takes place, along with the attainment of the limiting surface coverage at extremely low CB6 concentrations in solution. The CB6 adsorption occurs in a range from –1.9 to 0.2 V (*vs.* SCE), *i.e.*, at both positive and negative charges of the electrode surface [the potential of zero charge (PZC) in the background solution is –0.44 V (*vs.* SCE)]. Such a strong extension of the CB6 adsorption region into the region of negative potentials, as compared to the one of common neutral organic molecules (the region of their adsorption is usually ~1 V long and is situated in the vicinity of PZC[9]), indicates that the species adsorbed in this potential region are positively charged. A sharp increase in the capacitance at the most negative accessible potentials (*ca.* –1.9 V) is probably associated with the beginning of the electrochemical reduction of Na^+ cations in addition to adsorbate desorption. At the same time, the positive boundary of the CB6 adsorption region is ~0.5 V more positive than PZC, which makes it possible to assume that the adsorption layer is rearranged near this boundary. The same conclusion follows from the shape of *C vs. E* curves (Figure 1), which exhibit two regions corresponding to opposite charges of the electrode surface. Henceforth, we designate adsorption regions at the negative and positive electrode surface charges as regions I and II, respectively. It is evident that the formation of adsorbate layers in these regions proceeds at different rates (Figure 2): on the negatively charged surface, a change in electrode exposure time at each potential had no effect on the values of *C* (only limiting capacitance values are observed), whereas the adsorption-layer formation on the positively charged surface was slowed down. Moreover, note that the slowest process was observed when the potential was varied from positive to negative values. This may be explained by the fact that, in this case, equilibrium values

† The studies were carried out with a hanging mercury drop electrode by measuring the differential capacitance *C* as a function of potential *E* by means of an Autolab potentiostat-galvanostat at the frequency *f* = 370 Hz and an ac voltage amplitude of 1 mV. The working electrode potential was varied in steps of 20 mV. The *C vs. E* curves were recorded with electrode exposures at each potential (*t* = 2–30 s). A mercury drop with a surface area of 0.015 cm^2 (determined by weight) was formed at the end of a conical capillary with an inner diameter of 80 μm by means of a PA-3 polarographic analyzer (Czechoslovakia). The electrode potentials were measured with respect to a saturated calomel electrode. Cucurbit[6]uril (Fluka) was used without additional purification, Na_2SO_4 was twice crystallized and annealed at 500 °C, and water was cleaned on a Millipore unit. Solutions were deaerated with high purity argon.

Table 1 Adsorption parameters of the complex formed in a solution of cucurbit[6]uril + Na_2SO_4.

Electrode potential range / V	ϕ_m / V	ln B_m	A / μJ cm^{-2}	$\Gamma_m \times 10^{10}$ / mol cm^{-2}	$-\Delta G_m^a$ / kJ mol^{-1}	a_m	a_{m1}	C_m / μF cm^{-2}	C_{m1} / μF cm^{-2} V^{-1}	ϕ_N / V	Δ (%)
–0.2 to +0.3 region II	0.18	12.0	0.25	1.0	39.7	2.0	1.4	13.5	9.8	–0.32	18.4
–1.9 to –0.34 region I	–0.16	22.4	0.52	2.1	65.5	3.4	0	6.5	–2.0	0.53	8.8

[a]The free energy of adsorption $\Delta G_m$was determined from the expression $\Delta G_m = -RT\ln(55.5\,B_m)$.

were attained with the simultaneous involvement of diffusion and adsorbate layer formation. In contrast, when the potential was scanned in an opposite direction, a change in the sign of the electrode surface was accompanied by only a transformation of the adsorption layer. Note that, under equilibrium conditions, this transformation produces a stable adsorbate layer, as indicated by the appearance of a step in the *C vs. E* curve. Furthermore, the capacitance corresponding to this step is approximately twice as high as that in the region of negative surface charges. Presumably, this corresponds to a twofold change in the adsorption layer thickness. In contrast to CB5, CB6 does not form stable adsorption layer at the potential scanning to the negative direction. Its adsorption region therewith narrows down by 150–200 mV because of a negative shift of the positive boundary.

Thus, the above data indicate that, in the test systems, the properties of adsorption layers formed at the electrode/solution interface strongly depend on potential. Therefore, the parameters of these adsorbates were calculated using only a relevant part of the overall impedance data array. The calculations of the adsorption parameters were based on the model theory of the adsorption of organic substances[9] with the use of regression analysis.[10] We used the *C vs. E* dependence in a solution of 2.5×10^{-4} M CB6 + 0.1 M Na_2SO_4 measured for potential scanning to positive values and t = 20 s. The following parameters were used: the maximum adsorption potential ϕ_m in the rational potential scale; the logarithm of the adsorption equilibrium constant at a maximum adsorption potential ln B_m; the intermolecular interaction parameter in the adsorption layer a_m for $\phi = \phi_m$; the capacitance C_m at the limiting surface coverage with organic molecules (θ = 1) and $\phi = \phi_m$; the parameter $A = RT\Gamma_m$, where Γ_m is the limiting surface concentration of the organic substance for θ = 1 (R and T have their usual meaning); the parameters a_{m1} and C_{m1} describing the variation of the corresponding parameters with the potential. The parameter ϕ_N characterizing a change in the zero charge potential with the transition from θ = 0 to θ = 1 was found based on ϕ_m as described previously.[10]

Table 1 shows the CB6 adsorption layer parameters calculated for two potential regions. As follows from Figure 1 (inset), the calculations based on these parameters allowed us to adequately describe experimental *C vs. E* curves. The limiting capacitance and the adsorption for these layers differ considerably (by a factor of >2). For region II, Γ_m corresponds to the almost complete monolayer coverage on the electrode surface. The surface area per molecule found on this basis (1.66 nm^2) is close

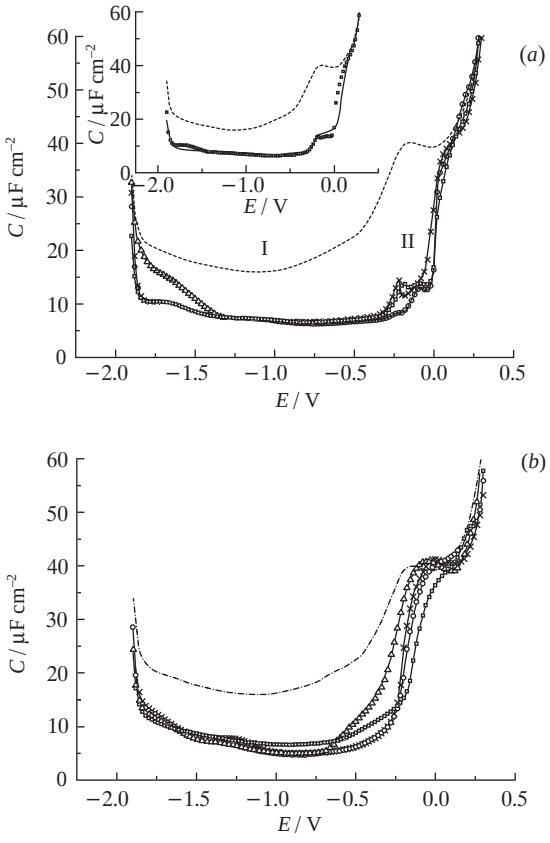


Figure 1 Experimental *C vs. E* curves of Hg electrode in 0.1 M Na_2SO_4 solution in the presence of CB6 in concentrations, M: (△) 10^{-5}, (×) 5×10^{-5}, (○) 10^{-4}, (□) 2.5×10^{-4}, obtained by potential scanning (*a*) from negative to positive and (*b*) from positive to negative *E* values. Electrode was held at every potential for 30 s. Inset: *C vs. E* curves in 0.1 M Na_2SO_4 in the presence of 2.5×10^{-4} M CB6: points refer to experimental data and lines were calculated with adsorption parameters obtained for the potential ranges of –1.9 to –0.34 V and –0.2 to +0.3 V. Dashed lines are the *C vs. E* curves in 0.1 M Na_2SO_4 solution.

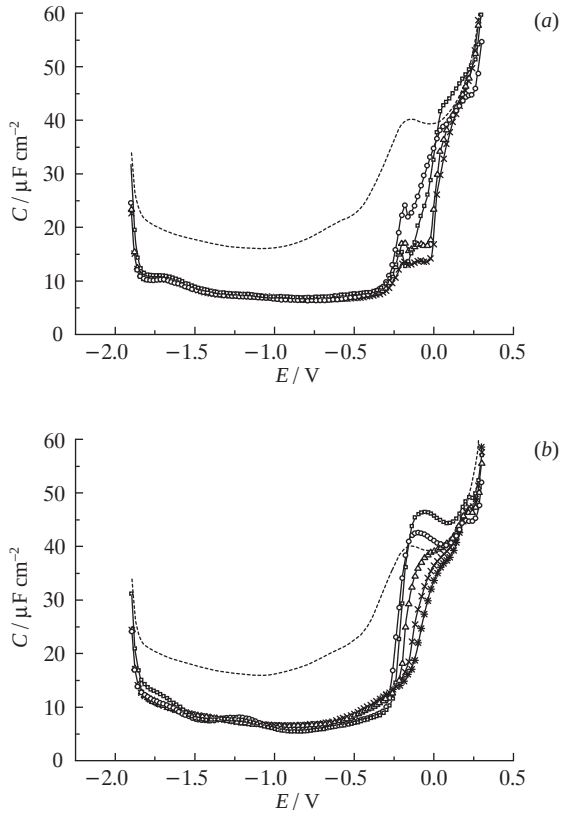


Figure 2 Experimental *C vs. E* curves of a Hg electrode in 0.1 M Na_2SO_4 solution in the presence of 2.5×10^{-4} M CB6, obtained by potential scanning (*a*) from negative to positive and (*b*) from positive to negative *E* values. Electrode was held at every value of potential for (○) 2, (□) 5, (△) 10, (×) 20 and (✳) 30 s.

to the value estimated from of the geometrical dimensions of CB6 molecules oriented to the surface with carbonyl oxygen atoms. This orientation was experimentally observed for adsorption from aqueous solutions on an uncharged gold surface.[4] It is evident that this is the way the neutral ligand molecule or its cationic complex should be oriented at positive surface charges. According to the estimations, in the test system, the number of free ligand molecules was almost two orders of magnitude smaller than the number of their complexes with sodium cation. The sodium complex with CB6 is the strongest among its complexes with other members of this homologous series. The sodium complex with CB5 is the weakest in this group. Accordingly, the CB5 + 0.1 M Na_2SO_4 system contains comparable concentrations of the ligand and its complex. It leads to the formation of an adsorption layer of CB5 molecules at positive electrode surface charges.[6] At the potentials more positive than the PZC in the test system the adsorption layer is formed by cationic CB6 complexes, probably due to the very low free ligand concentration, which can explain its desorption at the potentials much less positive as compared with the CB5 + 0.1 M Na_2SO_4 system.

The much faster formation of the adsorbate layer was observed at the negative electrode surface charges. In region I (excluding its boundary parts), the C values are independent of electrode exposure time at a given potential and of CB6 concentration. As follows from the tabulated data, in the latter region, the Γ_m value is twice as high as that in region II and the limiting capacitance is about a half of the corresponding value on the positively charged electrode surface. This can be explained by the formation of an adsorption bilayer in region I. Such a bilayer can be formed when, due to ion-dipole interactions, the Na^+ cation is simultaneously bound with oxygen portals of two CB6 cavitands one of which is localized immediately on the electrode surface and the other is oriented to the solution. The formation of such a bilayer structure was inferred[4] for the CB6 adsorption layer on gold in the presence of Na^+ cations. In the absence of these cations, *i.e.*, on the adsorption of neutral CB6 species, a monolayer was formed.[4] The large positive value of ϕ_N in region I points to the strong positive shift of PZC, *i.e.*, to the adsorption of the organic cation. The negative ϕ_N value in region II indicates that the adsorbed complexes are oriented with the carbonyl groups of CB6 portal to the electrode surface.

In the whole region of CB6 adsorption potentials, a_m remained positive, *i.e.*, attractive interactions between adsorbed species predominated. This interaction was the strongest at negative surface charges (region I). Note that, for the adsorption of CB5[6] and CB7, a_m takes negative values in region II and positive in region I, though much smaller as compared with CB6. Probably, this is explained by the fact that CB6 forms a stronger complex with the Na^+ cation, which may result in the greater screening of the cation charge and, correspondingly, the weakening of electrostatic repulsion between species within the adsorption layer.

The experimental data on the adsorption of cucurbiturils at the Hg electrode / 0.1 M Na_2SO_4 aqueous solution interface allow us to make preliminary conclusions on their adsorption properties such as a high surface activity, an unusually wide adsorption region and the formation of two adsorption layer structures. At the negative charges, the formation of an adsorption layer with the bilayer structure is most probable.

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