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Adsorption phenomena in solutions of cucurbit[6]uril in the presence of magnesium sulfate

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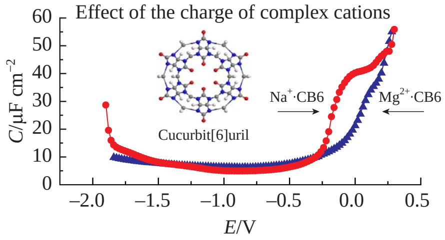
The behavior of cucurbit[6]uril at the electrode/solution interface in the presence of magnesium sulfate was investigated and quantified. It has been established that at the highest positive potential available for the adsorption of organic compounds, a structure is formed that consists entirely of neutral cavitand molecules.



Keywords: supramolecular complexes, cucurbit[6]uril, adsorption properties, $MgSO_4$ solutions, electrode potential, differential capacitance, stability constant.

Cucurbituril (CBn) series compounds represent a relatively new class of molecular containers. Their pumpkin-like molecules, composed of glycoluril fragments (the n in CBn is the number of such fragments), have a wide hydrophobic cavity and two portals framed by carbonyl groups. This allows them to form supramolecular complexes with inorganic cations due to their interaction with hydrophilic groups of portals and at the same time enclose organic compounds in the hydrophobic cavity. This feature, along with other unique properties of these cavitands, such as their rigid framework, high selectivity in the formation of complexes, solubility in aqueous solutions and essential nontoxicity, attract the attention of scientists from various fields of fundamental and applied science.[1–6]

The study and application of these cavitands is often carried out in systems containing interfaces. Published works emphasize that to fully characterize such systems, it is necessary to take into account the adsorption properties of the compounds that form them. Until recently, these data were practically absent, and only rare results merely stated the presence of adsorption in such systems. The only systematic investigation of this kind was a series of works in which, using impedance measurements, the characteristics of adsorption layers formed at the interface of a model Hg electrode with solutions of supramolecular cationic complexes of CBn (n = 5–8) were determined.[7,8] A more complete list of references to such works is contained in the cited article.[8] The bulk of the data was obtained for complexes of singly charged alkali metal cations. The first results for doubly charged cations were obtained in the Sr^{2+}–CBn system.[†,9]

The purpose of this work is to continue the study of adsorption phenomena in CBn solutions in the presence of salts of multiply charged cations for the particular case of the CB6–$MgSO_4$ system. As has been shown in previous studies, the interval of adsorption potentials of supramolecular cationic complexes consists of two regions. In a region more negative than the potential of zero charge (PZC), the cationic complexes are predominantly adsorbed, while in a region more positive than the PZC, a mixed adsorption layer is formed, consisting of these complexes and free ligand molecules. In this case, the overall picture of adsorption phenomena substantially depends on the stability of these complexes and the concentration of the components involved in their formation.

Although there are no published data on the stability of the Mg^{2+}·CB6 complex, our results showing that the solubility of this cavitand increases in magnesium sulfate solutions clearly confirm the formation of this complex. This is also evidenced by a comparison of the *C vs. E* dependence measured under the same conditions in 0.1 M solutions of $MgSO_4$ and Na_2SO_4 in the presence of 10^{-4} M CB6 (Figure 1). These results show that for $MgSO_4$ solutions containing CB6, the interval of adsorption potentials consists of two regions. Comparison of these data revealed their significant differences in the shape of the *C vs. E* dependences and the width of the adsorption region. For a sodium sulfate solution, the interval of adsorption potentials was narrower by ~0.2 V, and the capacitance *C* changed more sharply when scanning the potential in the positive direction. It is well known that the complex Na^+·CB6 with a stability constant $\log K = 3.49$ is the most stable among the complexes formed by alkali metal cations with CBn ligands.[10] Accordingly, solutions of this complex contain the lowest concentration of free cavitand CB6 (3×10^{-7} M for the system in Figure 1). This prevents the formation of a mixed

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[†] Electrochemical studies were carried out on an electrode in the form of a hanging mercury drop by measuring the differential capacitance *C* as a function of the potential *E* using a Metrohm Autolab potentiostat-galvanostat with a FRA module (Netherlands) at a frequency $f = 370$ Hz and an ac voltage amplitude of 1 mV. The working electrode potential was changed in steps of 20 mV. Curves of *C vs. E* were recorded at an electrode exposure time $t = 3–30$ s for each potential value. A drop of mercury with a surface area of 0.015 cm^2 (determined by the mass of several drops) was formed at the end of a conical capillary with an inner diameter of 80 μm using a special tool included in the PA-3 polarographic analyzer (Czechoslovakia). Electrode potentials were measured and reported relative to the AgCl electrode. Cucurbit[6]uril (CB6) was purchased from Fluka and used without further purification, $MgSO_4$ was crystallized twice, and the water was purified using a Millipore filter. The solutions were deaerated with high-purity argon.

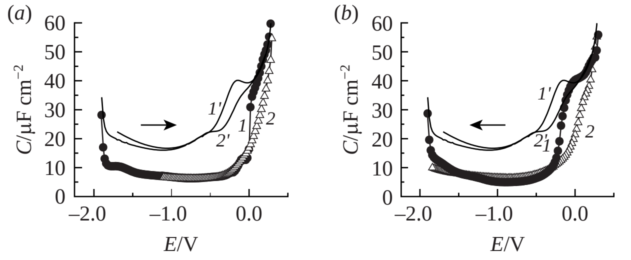

Figure 1 Experimental *C vs. E* curves for Hg electrode obtained by scanning the potential in (*a*) positive and (*b*) negative directions, in solutions (*1*),(*2*) with 10^{-4} M CB6 and (*1′*),(*2′*) without CB6 in the presence of (*1*),(*1′*) 0.1 M Na_2SO_4 and (*2*),(*2′*) 0.1 M $MgSO_4$. The electrode was held at each potential value for a time *t* = 30 s.

adsorption layer of CB6 and $Na^+{\cdot}CB6$, which sharply desorbs when the potential shifts in the positive direction. The results of studying this system showed that at *E* (*vs.* SCE) ⩾ 0 V, an adsorption layer does not form, since the concentration of free cavitand is approximately three orders of magnitude lower than the concentration of the cationic complex. This is why the adsorption region in this system is significantly narrower, and the *C vs. E* dependence at the positive adsorption limit has a peculiar shape. A considerable shift of this limit towards positive potentials for a system containing $Mg^{2+}{\cdot}CB6$ [Figure 1(*a*),(*b*), curves *2*] suggests that the concentration of free cavitand molecules is sufficient for the formation of a mixed adsorption layer, *i.e.*, the stability of this cationic complex is relatively low.

The above comparison was made for a CB6 concentration of 10^{-4} M and potential exposure time *t* = 30 s. It was of interest to carry out such a comparison for smaller values of the last parameter. It has been shown[7] that such systems are characterized by considerable temporary effects, which, as a rule, are more pronounced when scanning the potential in the negative direction and at relatively low cavitand concentrations. The appearance of such an effect, which causes differences in the shape of the *C vs. E* dependences measured in opposite directions of potential scan, may be associated with the hindered formation of adsorption layers of different compositions during adsorption/desorption processes.

It is evident that when scanning the potential in a negative direction at the initial stage of adsorption (positive potentials), free cavitand molecules appear first on the electrode surface, since the conditions for their adsorption are more favorable. With a further shift in potential, these molecules can form a mixed adsorption layer together with cationic complexes. The composition and structure of this mixed layer can vary depending on the potential and time of its exposure and are determined by the stability of these complexes and the ratio of concentrations of complexation reaction components. At relatively low concentrations of cavitand, when the positive limit of the adsorption region is shifted towards negative potentials, the adsorption of cationic complexes is also possible at the initial stage if the carbonyl groups on their portals are oriented towards the electrode surface. With a further shift of the potential in the negative direction, the adsorption layer should obviously be enriched with complex species oriented with magnesium cations towards the electrode surface. In the region of higher negative potentials, such an orientation appears to be the only possible one.

When the potential shifts in a positive direction, the desorption process first involves an adsorbate layer formed at more negative potentials and facing the electrode surface with metal cations. With a further shift of the potential in the positive direction, *i.e.*, into the transition region, the structure of the adsorption layer probably changes smoothly, gradually becoming enriched in neutral cavitand molecules and depleted in cationic complexes, which are reoriented as positively charged components are removed from the electrode surface.

For the $MgSO_4$–CB6 and Na_2SO_4–CB6 systems, the *C vs. E* dependences were compared for opposite potential scanning directions and different holding times *t* at each potential. It was shown that when moving towards positive potentials, accompanied by the desorption of adsorbed layers formed earlier at high negative potentials, the restructuring of these layers during the desorption process is not fast enough, so that at *t* ⩾ 10 s the value of *C* ceases to change (not shown). When scanning the potential in the negative direction, *i.e.*, during the initial formation of the adsorbate layer at positive potentials, sufficient differences are observed in the *C vs. E* curves for these systems [Figure 2(*a*),(*b*)]. It should be noted that for the Na_2SO_4–CB6 system the adsorption layer is formed much more slowly due to the extremely low concentration of the free cavitand. Moreover, in the studied range of *t* values (5–30 s), the limiting value *C* is not reached. The difference in the *C vs. E* dependences measured at different *t* is explained by the different structure and composition of the adsorption layer. It is obvious that at low *t* (5 s) and low concentration of free cavitand ($[CB6]^{free}$), a mixed adsorbate layer formed by cationic complexes and neutral CB6 molecules does not have time to form. Under these conditions, at $E \approx -0.25$ V, a sharp decrease in capacitance is observed, which corresponds to the instantaneous adsorption of only cationic complexes [Figure 2(*b*), curve *1*]. As noted earlier, for such systems $E \approx -0.25$ V is the limit of the existence of adsorption (essentially condensed) layers formed by supramolecular cationic complexes of this type.[11] At longer times *t*, conditions arise for the formation of a mixed adsorption layer, which leads to a decrease in capacitance and an extension of the adsorption region. For the Na_2SO_4–CB6 system, the positive limit of this region corresponds to $E \approx 0.0$ V.

For the $MgSO_4$–CB6 system, the formation of the adsorption layer occurs much faster, so that even at *t* = 30 s almost equilibrium values of *C* are observed [Figure 2(*a*)]. A considerable difference

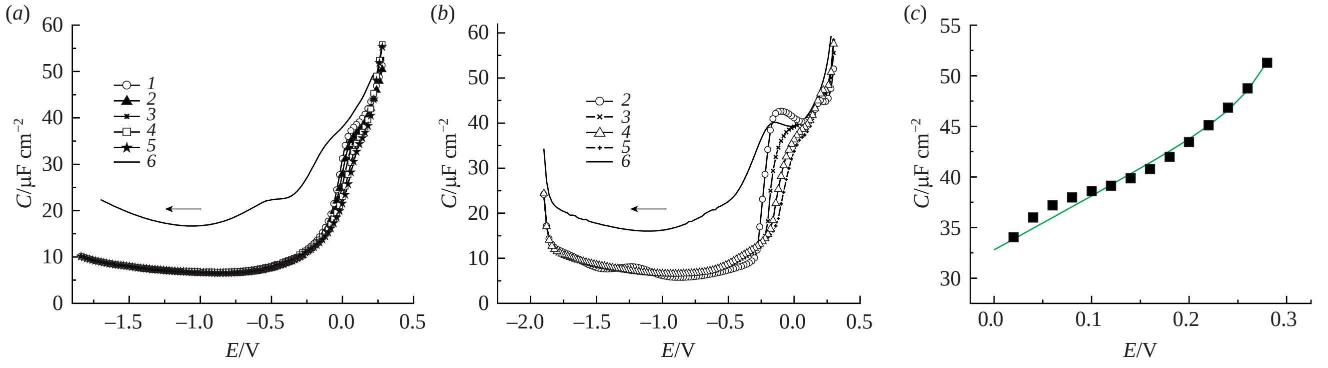

Figure 2 Experimental *C vs. E* curves for Hg electrode obtained by scanning the potential in the negative direction in solutions of (*a*) 10^{-4} M CB6 + 0.1 M $MgSO_4$ and (*b*) 2.5×10^{-4} M CB6 + 0.1 M Na_2SO_4, with the electrode held at each potential value for a time *t* of (*1*) 3, (*2*) 5, (*3*) 10, (*4*) 20 and (*5*) 30 s, compared with (*6*) *C vs. E* curves in solutions of (*a*) 0.1 M $MgSO_4$ and (*b*) 0.1 M Na_2SO_4. (*c*) *C vs. E* curve (line) for a solution of 10^{-4} M CB6 + 0.1 M $MgSO_4$, calculated using adsorption parameters obtained from experimental data at *t* = 5 s (symbols) in the potential range from +0.3 to 0.0 V.

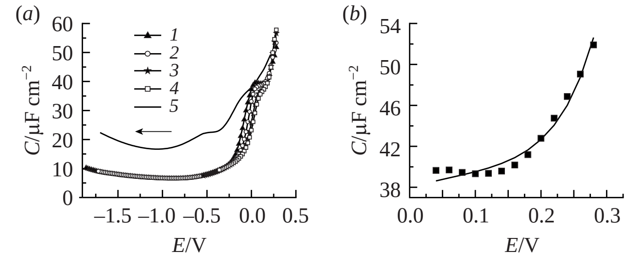

Figure 3 (*a*) Experimental *C vs. E* curves for Hg electrode obtained by scanning the potential in the negative direction in a solution of 5×10^{-5} M CB6 + 0.1 M $MgSO_4$, with the electrode held at each potential value for a time *t* of (*1*) 5, (*2*) 10, (*3*) 20 and (*4*) 30 s, compared to (*5*) the *C vs. E* curve in a solution of 0.1 M $MgSO_4$. (*b*) *C vs. E* curve (line) for a solution of 5×10^{-5} M CB6 + 0.1 M $MgSO_4$, calculated using adsorption parameters obtained from experimental data at *t* = 5 s (symbols) in the potential range from +0.3 to 0.0 V.

from the Na_2SO_4–CB6 system is also that the adsorption region is significantly extended up to $E \approx 0.3$ V. This can only be explained by an increase in the concentration $[CB6]^{free}$, which favors the formation of mixed adsorption layers. As can be seen, at $E > 0.0$ V, small steps are formed on the *C vs. E* curves at small *t*, which may point to the formation of certain relatively stable structures of the adsorption layer. As *t* increases, the capacitance *C* decreases in this region and the steps disappear. This effect can be explained by the gradual incorporation of complexes $Mg^{2+}\cdot CB6$ into the adsorption layer, initially formed by neutral CB6 molecules or maximally enriched with them. It is interesting that at $E > 0.2$ V all *C vs. E* dependences measured at different *t* coincide. Most probably, the decrease in *C* in this potential region compared to the background curve corresponds to the adsorption of only free CB6 molecules, while its cationic complexes cannot take part in the formation of the adsorbed layer at such positive potentials. Apparently, a decrease in the initial (total) cavitand concentration should also slow down the further incorporation of cationic complex species into the adsorbed layer formed by cavitand molecules. Accordingly, the formation of steps in the *C vs. E* curves should be more pronounced. This is confirmed by the *C vs. E* dependences [Figure 3(*a*)], corresponding to the formation of an adsorption layer at a CB6 concentration of 5×10^{-5} M and various *t*. As can be seen, at *t* = 5 s, the *C vs. E* dependence contains a well pronounced step, which at $E \sim 0.0$ V coincides with the *C vs. E* dependence in a solution of the supporting electrolyte, which actually means desorption of the adsorbate. As was described earlier for a solution containing 10^{-4} M CB6 [see Figure 2(*a*)], capacitance *C* decreases with increasing *t* and this step almost disappears. It can be assumed that the appearance of this step in the *C vs. E* dependences may be associated with the formation of some new form of adsorption layer, different from the one that is formed at more negative potentials and, probably, built only from neutral CB6 molecules. The region of existence of this form is localized at more positive potentials of the adsorption region and is limited on one side by the potential for complete removal of organic species from the electrode surface (about 0.3 V) and on the other side by the potential of a characteristic change in the *C vs. E* dependence, marking the beginning of the formation of the adsorption layer involving cationic complexes. For low concentrations of cavitand and small *t*, when the formation of the adsorption layer exclusively by CB6 molecules is most probable, this limit corresponds to about 0.0 V; for higher concentrations of CB6 and values of *t*, this limit shifts in the positive direction.

It would be very interesting to quantify these adsorption layers formed at the highest positive potentials available for this system. Since the stability constant *K* of the $Mg^{2+}\cdot CB6$ complex is unknown, the concentrations of free molecules $[CB6]^{free}$ required for such calculations were found using the value lg*K* = 2, which is the average value for several complexes of doubly charged metal cations with CB6.[‡,12] For 0.1 M $MgSO_4$ solutions containing 1×10^{-4} and 5×10^{-5} M CB6, we obtained $[CB6]^{free}$ concentrations of 1×10^{-5} and 5×10^{-6} M, respectively. From these values, the adsorption parameters were calculated for the adsorbate layer formed on the electrode at minimum times of exposure to potential in the range of 0.3–0.0 V. This calculation was carried out using a method[13] based on regression analysis of adsorption data. In this case, the equations of the model theory of reversible adsorption of organic compounds on electrodes, based on the Frumkin isotherm, were used:

$$Bc = [\theta/(1-\theta)]\exp(-2a\theta),$$

where *B* is the adsorption equilibrium constant, *c* is the volume concentration of organic matter, θ is the degree of surface filling with organic matter, and *a* is a parameter characterizing the interaction between adsorbed particles. It was shown[14] that this isotherm is optimal for obtaining parameter values that characterize the properties of adsorption layers of organic compounds and allow a quantitative description of experimental data.

The experimental data were processed using the following parameters: the logarithm of the adsorption equilibrium constant $\ln B_m$ at the maximum adsorption potential φ_m in a rational potential scale; the parameter of intermolecular interaction in the adsorption layer a_m for $\varphi = \varphi_m$; the capacitance C_m at the limiting surface coverage with organic molecules ($\theta = 1$) and $\varphi = \varphi_m$; the parameter Γ_m, which is the limiting surface concentration of the organic substance for $\theta = 1$; the parameter φ_N, characterizing the change in the PZC with the transition from $\theta = 0$ to $\theta = 1$; the parameter C_{m1}, which describes the variation of this quantity with potential.

The data obtained (Table 1) should be considered preliminary; however, as will be shown below, in principle they can provide a reliable and consistent description of adsorption layers in this potential range. It is worth mentioning that at a lower concentration of CB6, the calculations turned out to be feasible with a minimum number (5) of adsorption parameters, which indicates a certain stability of the adsorption layer.

For the higher concentration of CB6, the additional parameter C_{m1} should be taken into account, which describes the change in capacitance with a change in potential. As can be seen [Figure 2(*a*), curve *1*], for this system such changes are indeed more pronounced. A common feature of the adsorption layers in both systems is the low degree of coverage of the electrode surface. On average, it is 0.34×10^{-10} mol cm^{-2} (~480 Å^2 per molecule), while with complete surface coverage $\Gamma_m = 1\times10^{-10}$ mol cm^{-2} (~163 Å^2 per molecule). It can be assumed that with the higher initial concentration of CB6 and, accordingly, the larger number of CB6 molecules on the surface, favorable conditions arise for the incorporation of cations (Mg^{2+} and $Mg^{2+}\cdot CB6$) into the layer, which leads to corresponding changes in adsorption parameters. Thus, an increase in CB6 concentration leads to an increase in φ_N, *i.e.*, to a stronger shift in PZC in the positive direction. Also, a shift in a_m towards positive values is observed and can be explained by the fact that the presence of positively charged species in the adsorption layer helps to reduce the repulsive interaction between neutral CB6 molecules, which have two portals framed by negatively polarized carbonyl groups. Probably, in the absence of cationic complexes, neutral CB6 molecules cannot form a sufficiently dense adsorption layer, which follows from the negative values of a_m in the adsorption layer formed at the positive limit of the

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[‡] The value of *K* required for more accurate calculations for the $Mg^{2+}\cdot CB6$ complex can be obtained (in our further studies) using, for example, the method proposed in a recently published work,[8] which consists of comparing the impedance data for two very similar systems, differing only in that the first contains the complex we are interested in, and the second contains some other complex with a known stability constant.

Table 1 Parameters of adsorption layers formed in solutions of CB6 + 0.1 M $MgSO_4$ in the range of electrode potentials from +0.3 to 0.0 V.

Entry	[CB6]/M	$[CB6]^{free}$/M	$\ln(B_m/dm^3\ mol^{-1})$	$\Gamma_m/10^{-10}$ mol cm^{-2}	$-\Delta G_m$/kJ mol^{-1}	a_m	C_m/μF cm^{-2}	C_{m1}/μF cm^{-2} V^{-1}	φ_N/V	Δ(%)
1	1×10^{-4}	1×10^{-5}	14.4	0.32	46.6	0.54	31.0	53.1	0.19	2.6
2	5×10^{-5}	5×10^{-6}	11.5	0.36	38.4	−0.90	37.4	0.0	0.04	1.9

adsorption region at t = 3 s, *i.e.*, under conditions that maximally exclude the involvement of positively charged species in the formation of the adsorption layer.

Using the found parameters, we calculated the corresponding sections on the curves of C *vs*. E dependences. Comparison of the obtained results with experimental data demonstrated their adequate agreement [Figures 2(*c*) and 3(*b*)]. In general, despite the not very strict nature of our assessment of the adsorption parameters of adsorbate layers at the maximum positive electrode potentials possible for the CB6–$MgSO_4$ system, the results obtained made it possible to quantitatively describe the observed phenomena in a first approximation and give their consistent explanation.

In summary, the existence of a new structure of the adsorption layer at the interface between the electrode and solutions of cationic complexes of cucurbiturils has been established. Most likely, this structure consists entirely or almost entirely of neutral cavitand molecules.

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