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Mendeleev Commun., 2018, **28**, 281–283

Mendeleev Communications

Properties of cucurbit[8]uril adsorption layer at the electrode/solution interface

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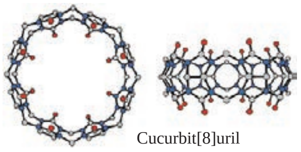
DOI: 10.1016/j.mencom.2018.05.017

Studies and quantification of cucurbit[8]uril properties at the electrode/solution interface in a wide range of the electrode potential and adsorbate concentration revealed features of its adsorption behaviour. It forms a mixed adsorption layer similar to cucurbit[7]uril, while cucurbit[6]uril does not.



Cucurbit[8]uril

Cucurbit[8]uril (CB8) pertains to a promising homologous series of macrocyclic cavitands. They were named so because their molecules resemble a pumpkin. The first compound from this class (cucurbit[6]uril) was synthesized in 1905.[1] However, the structure of such molecular capsules, which determines their unique properties, was elucidated only in 1981.[2] Cucurbiturils contain strongly hydrophobic intermolecular cavities with portals framed by carbonyl groups. Such unique combination allows cucurbiturils to form both inclusion compounds with organic ‘guest’ molecules of the appropriate size and complexes with metal cations. The recent active studies of these compounds were focused on prospects of their application in supramolecular chemistry, medicine, biochemistry, and nanotechnology.[3,4]

Published reports contain information about an adsorption of cucurbiturils and their complexes on a surface of certain metals and oxides.[3,4] However, the correct interpretation and analysis of such results are impossible without the data on the properties of the formed adsorption layers. Systematic studies in this field were started recently by our group, which allowed us to obtain quantitative characteristics for the adsorption layers formed by CB5, CB6, and CB7 on the Hg-electrode/solution interface.[5–7,†]

This work was aimed at the investigation of the CB8 adsorption at the interface Hg-electrode/0.1 M Na_2SO_4 solution. The outer diameter and the height of the CB8 molecule are 1.75 and 0.91 nm, respectively. The diameter of its internal cavity is 0.88 nm, and its volume is 0.479 nm^3. The solubility of CB8 in water is very low (~10^{-6} mol dm^{-3}) but increases considerably upon addition of ammonium, alkali, and alkali-earth metal salts due to a formation of complexes. With the Na^+ cation, CB8 forms the complex with the 1:1 composition and the stability constant $\lg K_s = 2.62$.[3] The differential capacitance *vs*. potential (*C vs*. *E*) curves were recorded for the mercury electrode in 0.1 M Na_2SO_4 aqueous solutions containing CB8 at concentrations from 10^{-5} to 10^{-6} mol dm^{-3}. Figure 1 shows the *C vs*. *E* curves for the system containing 10^{-5} mol dm^{-3} CB8, recorded in opposite potential-scan directions for different times of electrode exposure at each potential value. It is evident that CB8 should have the adsorption

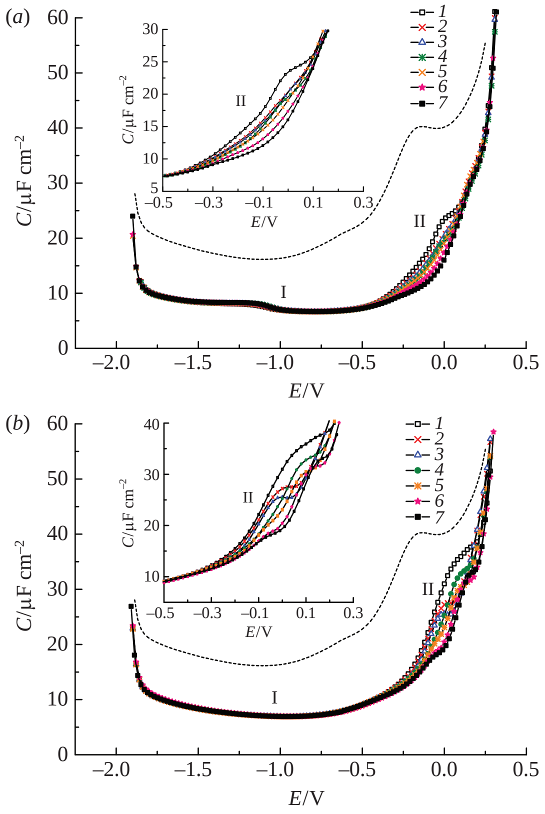


Figure 1 Experimental *C vs*. *E* curves for Hg electrode in 0.1 M Na_2SO_4 solution in the presence of CB8 (10^{-5} mol dm^{-3}) for *t*: (*1*) 0.5, (*2*) 1, (*3*) 3, (*4*) 5, (*5*) 10, (*6*) 15, and (*7*) 35 s obtained by potential scanning (*a*) from negative to positive and (*b*) from positive to negative *E* values. Hereinafter, the dashed lines represent the *C vs*. *E* curves in 0.1 M Na_2SO_4. The insets show regions II on an enlarged scale.

[†] The hanging mercury drop electrode was used in the measurements of the differential capacitance *C* as a function of potential *E* on an Autolab potentiostat-galvanostat at 370 Hz and ac voltage amplitude of 1 mV. The working electrode potential was varied by 20 mV steps. The *C vs*. *E* curves were recorded with electrode exposure at each potential (*t* = 0.5–35 s). A mercury drop with the surface of 0.015 cm^2 (determined from the weight of several drops) was formed at the end of a conical capillary with the inner diameter of 80 μm using a special tool included in the polarographic analyzer PA-3. The electrode potentials were measured with respect to a saturated calomel electrode. Cucurbit[8]uril (Fluka) was used without additional purification, Na_2SO_4 was twice recrystallized and annealed at 500 °C, water was cleaned on the Millipore unit. Solutions were deaerated with high purity argon.

behaviour similar to those of studied earlier CB5, CB6, and CB7.[5–7] In the presence of CB8, a remarkably wide adsorption region was observed (~2 V), wherein *C* values were lower in comparison with the supporting electrolyte solution containing no CB8 (the adsorption region of common neutral organic compounds does not usually exceed 1 V[8]). Similar to the other homologues, in case of CB8, the limiting electrode surface coverage with the adsorbate was reached at the extremely low concentrations. According to Figure 1, the *C vs. E* dependences demonstrate two regions with different *C* values, which may indicate the formation of adsorption layers having different structures. The transition between these regions occurs near the potential of zero charge (PZC) for this electrode in the supporting electrolyte solution (~0.44 V). This observation allows one to assume that the potential variation in this region is accompanied by certain changes in the charge of adsorbed species. The negative boundary of the CB8 adsorption potential region corresponds to *ca*. –1.85 V, *i.e*., its largest part (~1.4 V) pertains to the negatively charged electrode. This can suggest that the positively charged species were adsorbed at this region. Therefore, we assumed that a complex of CB8 with the Na^+ cation was adsorbed on the electrode surface by analogy to other homologues. The positive charge of the above species should prevent its adsorption at the positive charges of the electrode; however, the positive boundary of the adsorbate layer region is shifted with respect to PZC by ~0.7 V. This can be due to participation of the cucurbituril molecules in the formation of the adsorbate layer at this region.

One can designate segments in *C vs. E* curves corresponding to negative and positive surface charges as regions I and II, respectively. The adsorption layer formation differs substantially for these regions of *C vs. E* curve. While in region I, the capacitance values were virtually independent on the CB8 concentration, the time of electrode exposure at a given potential, and the potential scan direction; in region II, the mentioned dependences were observed, which resulted in the appearance of hysteresis. The acquired data showed that with extending the exposure, the *C* values in region II decreased down to the constant values at the exposure time *t* of ~20 s. Thus, the formation of the adsorbate layer in region II was slower than that in region I. This effect can be explained by the inhibited adsorption of cationic complexes on the positively charged electrode surface and by low concentrations of CB8, whose adsorption in this region was preferred due to the presence of carbonyl groups at its portals. In region II, when the potential was scanned in the negative direction, some steps appeared in the *C vs. E* curves, which could indicate the formation of certain relatively stable adsorbate structures in narrow potential regions. During the reverse potential scan, such steps were observed only for very small *t* values, *i.e*., for the low surface coverages by adsorbed molecules. The revealed differences in the adsorbed layer formation for the opposite potential scans can be related to the fact that the transformation of the formed earlier adsorbed layer was observed in region II for the negative scan, while during the reverse scan the adsorption layer was formed coincident with the delivery of adsorbate molecules to the electrode surface. These effects were similar to the previously reported adsorption properties of cucurbiturils. Thus, the acquired data suggest that the layer formation on the electrode surface substantially depends on the potential in this system. This was the reason for separated processing of the experimental data for regions I and II in order to find the adsorption parameters using the developed[9] method of regression analysis. The calculations were carried out for data arrays acquired on the 10^{-5} M CB8 solution in the opposite potential scans at the maximum *t* of 35 s. The experimental data were processed with the following parameters: the maximum adsorption potential φ_m on the rational potential scale; logarithm of the adsorption equilibrium constant at the maximum of adsorption potential $\ln B_m$; 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 $A = RT\Gamma_m$, where Γ_m is the limiting surface concentration of the organic substance for $\theta = 1$ (*R* and *T* have their usual meaning); the parameters a_{m1} and C_{m1} describing the variation related to the potential. The parameter φ_N characterizing the change at the zero charge potential during transition from $\theta = 0$ to $\theta = 1$ was determined from the φ_m value according to the known method.[9]

The comparison of results showed that the adsorption parameters were different for opposite scan directions. Moreover, the largest root-mean-square deviations between the calculated and experimental values revealed certain slowness in the adsorption layer formation during the initial period of measurements. Such effects have not been earlier observed for other cucurbiturils. Their appearance in case of the CB8 system was probably associated with the considerable ligand size, the lower rigidity of its structure, and the possible conformational changes upon potential variation. Thus, the most reliable results for region I were probably those obtained during potential scanning from positive to negative values. For region II, the reliable results were those obtained in the reverse scan (Table 1).

These results demonstrated a substantial dependence of the adsorption layer properties on the potential. The maximum adsorption values found for these layers were deviated widely, almost twofold. For region II, Γ_m could correspond to the complete surface coverage by the adsorbate. However, the occupied by one molecule in the monolayer surface area calculated from this Γ_m value with an assumption, that molecules had carbonyl groups oriented to the electrode surface, was smaller than the area corresponding to the geometrical size of CB8. The found surface per molecule value in the adsorption layer means that the ligand radius decreased by 0.09 nm. This deviation can be explained either by some change in orientation or by certain contraction of the molecule in the adsorption layer, since the cucurbituril structure becomes less rigid with increasing the size of its molecule.

On the other hand, for the adsorbate layer that formed faster at the negatively charged surface, the Γ_m value was doubled while the limiting capacitance was almost half of its value in region II. This can be caused by the formation of an adsorption bilayer in region I. Such bilayer could be formed in case of simultaneous binding of the Na^+ cation with carbonyl groups belonging to the two CB8 molecules, one of which was attached to the electrode surface while the other was faced to the solution. The formation of such structures was observed for similar systems on gold.[10]

The parameters $\ln B_m$ and φ_N were close to the values found for CB7.[6] The increased value of parameter $\ln B_m$ in region I was associated with the contribution of electrostatic interaction between the cationic complex and charged electrode surface.

Table 1 Adsorption parameters for the complex formed in solutions containing cucurbit[8]uril and Na_2SO_4.

Electrode potential range/V	φ_m/V	$\ln(B_m$/ $dm^3\,mol^{-1})$	*A*/ $\mu J\,cm^{-2}$	Γ_m/ 10^{10} mol cm^{-2}	$-\Delta G_m{}^a$/ kJ mol^{-1}	a_m	a_{m1}	C_m/ $\mu F\,cm^{-2}$	C_{m1}/ $\mu F\,cm^{-2}\,V^{-1}$	C_{m2}/ $\mu F\,cm^{-2}\,V^{-2}$	φ_N/V	Δ (%)
–1.9 to –0.5 (region I)	–0.58	16.9	0.5	2.0	51.8	1.8	0	6.9	0	5.9	0.53	1.6
–0.18 to +0.3 (region II)	0.36	11.8	0.24	1.0	39.2	3.4	–42	12.7	19	0	–0.58	0.9

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

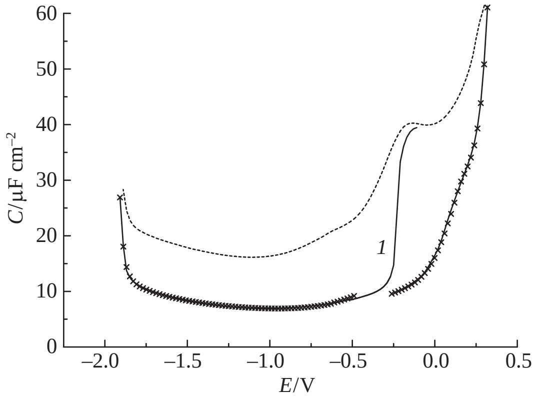


Figure 2 C *vs*. E curves in 0.1 M Na_2SO_4 solution in the presence of CB8 (10^{-5} mol dm^{-3}): the points are referred to the experimental data, while lines were calculated for the adsorption parameters given in Table 1.

Subsequently, the parameter φ_N was positive. In region II, the latter parameter changed its sign due to the cavitand orientation with carbonyl groups directed to the electrode surface.

The values of parameter a were considerably different from those for CB7. Its high positive values indicated a formation of the condensed adsorption layer in both regions. This may be explained by a denser packing of species in the adsorption layer, associated with the less rigid structure of CB8 molecule.

Figure 2 illustrates comparison between the C *vs*. E dependences found experimentally and calculated with these parameters. These curves are in adequate agreement with each other. Curve *1*, which was simulated for the wider potential range than that in calculations of parameters, corresponds to the hypothetic case when only the cationic complex was adsorbed on the electrode. In such a case, the adsorption would occur in the narrower potential interval as compared with that observed in the performed experiments. As noted above, that the extended adsorption region in the studied system could be associated with the formation of a mixed adsorption layer formed by both CB8 and its cationic complexes.

It was worthwhile to compare the obtained experimental C *vs*. E dependence with those measured earlier for several cucurbituril homologues (Figure 3). The observed deviations were mainly related to the region of positive electrode surface charges. In case of CB6, the adsorption region was narrower than those for CB7 and CB8 since its positive limit was shifted by 0.25 V to negative potentials. This was caused by the higher stability of the CB6Na$^+$ complex ($\log K_s = 3.49$, *cf.* 2.89 and 2.62 for CB7 and CB8, respectively). Due to the very low concentration of free CB6 in solution (~10^{-8} mol dm^{-3}), its participation in the formation of a mixed adsorption layer with cationic complexes is virtually impossible. Thus, the formation of the adsorption layer containing the CB6Na$^+$ complexes, which desorbed at the much lower positive potentials in comparison with CB7 and CB8, was observed in a certain narrow potential region. In the systems containing CB7 and CB8, the formation of the mixed adsorption layers, which desorbed from the electrode surface at more positive potentials, became possible due to the lower stability of cationic complexes and, accordingly, the increased concentration of free ligands (> 10^{-7} mol dm^{-3}). Moreover, the C values for the CB8 adsorption were lower at the same potential, which was probably caused by its higher surface activity. Furthermore, the higher stability of the CB6Na$^+$ complex could explain the slower formation of its adsorption layer at the high negative potentials on the electrode surface. Apparently, the stronger screening of the cation charge by carbonyl groups weakened its electrostatic interaction with the electrode surface.

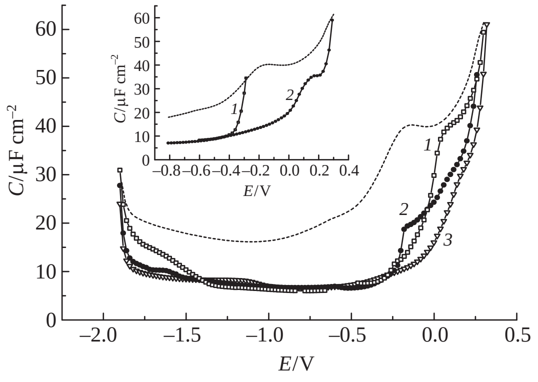


Figure 3 C *vs*. E curves in 0.1 M Na_2SO_4 solution in the presence of 10^{-5} mol dm^{-3} of (*1*) CB6, (*2*) CB7, and (*3*) CB8, obtained by potential scanning from negative to positive E values at t = 35 s. The inset shows C *vs*. E curves in 0.1 M Na_2SO_4 solution in the presence of 5×10^{-6} mol dm^{-3} of (*1*) CB7 and (*2*) CB8.

The comparison of C *vs*. E dependences for CB7 and CB8 at the concentration of 5×10^{-6} mol dm^{-3} (inset in Figure 3) allows one to conclude that in contrast to CB8, no adsorption layer was formed for CB7 in region II, *i.e*., only its cationic complexes were adsorbed at the negative electrode charges. Note that the concentrations of free ligands were approximately equal in these systems due to the close values of $\log K_s$. The positive limit of the adsorption region for CB7Na$^+$ corresponded to *ca*. –0.2 V. The adsorption region extension upon the transition from CB7 to CB8 was accompanied by the formation of the mixed adsorption layer evidently due to the higher surface activity of adsorbate species, which might be associated with the increased parameter a observed in this potential region for the CB8 system.

The obtained quantitative data on cucurbit[8]uril are a part of the complex investigation of the adsorption behavior of cavitands at the electrode/solution interface. It was shown that the main peculiarities of the adsorption layer formation by CB8 compound (the wide adsorption region, the high surface activity, the formation of two adsorption-layer structures) were similar to those found earlier for the other members of cucurbituril homologous series. However, comparison of data for cavitands of this family (from CB6 to CB8) reveals significant distinctions in their adsorption behaviour. This is due in particular to different stability of formed cationic supramolecular complexes, which can lead to the formation of mixed layers on the electrode surface as in the case of CB7 and CB8.

This work was supported by the Program of M. V. Lomonosov Moscow State University Development and the Russian Science Foundation (grant no. 14-13-00751).

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Received: 26h October 2017; Com. 17/5382