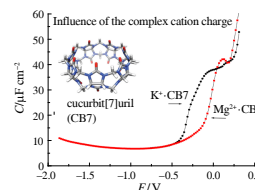# Adsorption phenomena in cucurbit[7]uril solutions in the presence of magnesium sulfate

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The behavior of cucurbit[7]uril in the presence of magnesium sulfate at the electrode–solution interface was explored and quantified. The comparison with the results for the MgSO₄–cucurbit[6]uril system obtained under the same conditions revealed their principal closeness.

The first member of the family of cucurbiturils as molecular containers was synthesized back in 1905;[1] however, the structure of these pumpkin-like molecules formed of n glycoluril fragments (CB_n series) with two symmetrical portals framed with carbonyl groups was determined only in 1981.[2] From this moment, interest in these compounds with unique properties[3–7] associated with their ability to form complexes simultaneously with organic compounds (by including them into a hydrophobic intramolecular cavity) and inorganic cations (through interaction with carbonyl groups at the portals) constantly increased. Today, cucurbiturils are used in different fields of fundamental and applied science (supramolecular chemistry, catalysis, pharmacology, and analysis and separation of mixtures).

The detailed characterization of the cucurbituril family requires information about their interfacial behavior. However, this kind of information is scarce in the literature. A cycle of our publications (see work[8] containing references to the main reports) comprises the results of systematic investigations of the adsorption phenomena at the interface formed by a Hg electrode with salt solutions containing CB_{n_s} (n = 5–8), where the supramolecular complexes with metal cations can be formed. This allows the parameters quantitatively characterizing the properties of adsorption layers formed at the interface to be determined. The main body of such data pertain to systems containing single-charged complexes of CB_{n_s} with alkali metal ions. Only two publications consider the adsorption phenomena in systems containing double charged cationic complexes of this type ($Sr^{2+}\cdot CB7$ and $Mg^{2+}\cdot CB6$).[9,10]

This work continues the investigation of the adsorption behavior of double charged cationic complexes of cucurbiturils by measuring the differential capacitance C as a function of the potential E.[†] We have chosen the MgSO₄–CB7 system having no

published information regarding the formation of complexes. Figures 1(*a*), 1(*c*), 2(*a*), and 2(*c*) display a series of *C vs. E* curves for 0.1 M MgSO₄ solutions in the presence of different concentrations of CB7 at different potential scan directions and exposure times (*t*). These results confirm the formation of $Mg^{2+}\cdot CB7$ complexes demonstrating the same principal features typical for the earlier described systems containing single-charged and double-charged complexes of CB_{n_s}, such as their remarkably wide adsorption region (~ 2 V) divided into two parts with the boundary corresponding to the potential of a zero charge (PZC) of the Hg electrode (−393 mV *vs.* Ag/AgCl). Similar to the systems of this type reported earlier, no *C vs. t* dependence is observed in the used interval of the time of electrode exposure at each potential (t = 1–30 s) in the region corresponding to the negative electrode surface charge where the adsorption layer is formed from supramolecular complex cations. In contrast, at the positive surface charges, such dependence is observed. In our earlier publications, this was explained by the formation of a mixed adsorption layer (MAdL), which included both cationic complexes and free cavitand molecules. This is the only approach that allows one to explain the extension of the adsorption region to such high positive potentials (~ 0.3 V) in systems containing cationic complexes under investigation.

The impedance data shown below for the MgSO₄–CB7 system compared with the corresponding data obtained earlier for the MgSO₄–CB6 system reveals their practical coincidence, which suggests that the stability constants (K) of the cationic complexes $Mg^{2+}\cdot CB6$ and $Mg^{2+}\cdot CB7$ are very close to one another. The data for magnesium sulfate solutions in the presence of 10^{-4} mol dm⁻³ CB7 reveal somewhat lower C values in the region of formation of MAdL compared to those for sodium sulfate solutions. This probably points to the lower stability of the complex $Mg^{2+}\cdot CB7$ compared with $Na^+\cdot CB7$ (lg K = 2.89).[11] In order to make more rigorous conclusions of this kind, one

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must compare close systems (the same electrolyte, the same charge of the cation).[8]

A more detailed comparison of the adsorption behavior of double-charged and single-charged cationic complexes of CB7 under analogous conditions was carried out for MgSO$_4$–CB7 and K$_2$SO$_4$–CB7 systems where the complex K$^+$·CB7 is formed.[12] Data for 0.1 M K$_2$SO$_4$ solutions in the presence of CB7 in different concentrations are shown in Figures 1(*b*), 1(*d*), 2(*b*), and 2(*d*), where the data for MgSO$_4$–CB7 at *t* = 30 s are also given, which allows one to compare data for these systems directly at large values of *t*. The lower limiting *C* values are observed for the MgSO$_4$–CB7 system [Figures 1(*b*), curve *5* and 1(*d*), curve *6*] in the negative potential region where no time dependences are observed in the chosen time interval, in its part adjacent to the negative boundary of the adsorption region, irrespective of the potential scan direction. It is probable that the layer of complexes Mg^{2+}·CB7 is bound stronger with the electrode than the layer formed from single-charged cationic complexes K$^+$·CB7 due to the stronger effect of electrostatic forces. It is seen that a more pronounced increase in the capacitance *C* with the increase in the negative potential value is observed for the K$_2$SO$_4$–CB7 system, which suggests that the adsorption layer formed of K$^+$·CB7 complexes is destructed more actively during the desorption process.

It should be noted that the time effects observed for the MgSO$_4$–CB7 system in the region of MAdL formation (positive electrode charges) are more pronounced than those for the K$_2$SO$_4$–CB7 system. Most probably, this is associated with the action of electrostatic forces that hinder the processes of formation/destruction of the mixed adsorption layer involving double charged cations. As a result, the limiting *C* values are not attained in this system for the 10^{-5} mol dm^{-3} CB7 concentration in the chosen *t* interval. At the 10^{-4} mol dm^{-3} CB7 concentration, this effect is observed only when the potential is scanned to its negative values (formation of MAdL in the course of diffusion of components from solution). At the same time, it deserves mention that in the narrow potential region (~ 0.2–0.3 V) adjacent to the positive limit of the region of adsorption of organic species, the *C vs. E* curves measured at different *t* merge together for both systems in both potential scan directions (Figures 1 and 2). The analogous effect
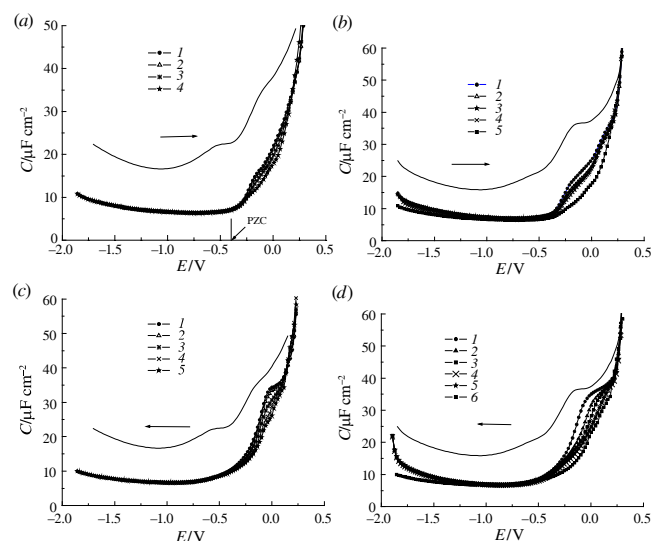

Figure 1 Experimental *C vs. E* curves for Hg electrode obtained by scanning the potential in (*a*, *b*) positive direction and in (*c*, *d*) negative direction in 10^{-4} M CB7 solutions in the presence of (*a*, *c*) 0.1 mol dm^{-3} MgSO$_4$ and (*b*, *d*) 0.1 mol dm^{-3} K$_2$SO$_4$. Electrode was held at each potential value for a time *t*: (*a*) (*1*) 3, (*2*) 5, (*3*) 10, and (*4*) 30 s; (*b*) (*1*) 1, (*2*) 5, (*3*) 10, and (*4*) 20 s; (*c*) (*1*) 3, (*2*) 5, (*3*) 10, (*4*) 20, and (*5*) 30 s; (*d*) (*1*) 1, (*2*) 5, (*3*) 10, (*4*) 20, and (*5*) 30 s. (*b*, curve *5*; and *d*, curve *6*) *C vs. E* in the presence of 0.1 mol dm^{-3} MgSO$_4$ for 30 s.
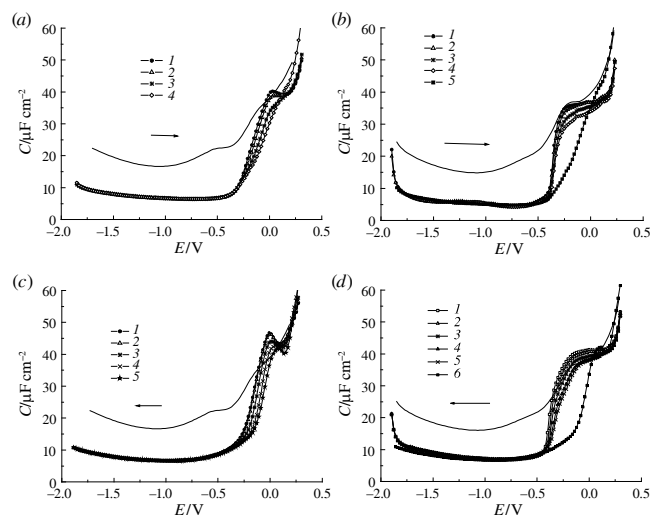

Figure 2 Experimental *C vs. E* curves for Hg electrode obtained by scanning the potential in (*a*, *b*) positive direction and in (*c*, *d*) negative direction in 10^{-5} M CB7 solutions in the presence of (*a*, *c*) 0.1 mol dm^{-3} MgSO$_4$ and (*b*, *d*) 0.1 mol dm^{-3} K$_2$SO$_4$. Electrode was held at each potential value for a time *t*: (*a*) (*1*) 3, (*2*) 5, (*3*) 10, and (*4*) 30 s; (*b*) (*1*) 1, (*2*) 5, (*3*) 10, and (*4*) 20 s; (*c*) (*1*) 3, (*2*) 5, (*3*) 10, (*4*) 20, and (*5*) 30 s; (*d*) (*1*) 1, (*2*) 5, (*3*) 10, (*4*) 20, and (*5*) 30 s. (*b*, curve *5*; and *d*, curve *6*) *C vs. E* in the presence of 0.1 mol dm^{-3} MgSO$_4$ for 30 s.

was observed in our previous work devoted to the MgSO$_4$–CB6 system.[10] It is probable that the potential of 0.2 ± 0.03 V, which is ~ 600 mV more positive than the PZC, determines the limit beyond which the cations (in any form) cannot longer remain on the electrode in the positive scan direction. Thus, the time-independent *C* values observed in this region correspond to the adsorption of free cavitand molecules.‡

Comparing the data for the MgSO$_4$–CB7 and K$_2$SO$_4$–CB7 systems obtained under various experimental conditions (at different CB7 concentrations, potential scan directions, and exposure times) reveals that in all the cases in the region adjacent to the positive limit of the adsorption region and corresponding to the formation of the mixed adsorption layer, the lower *C* values are observed invariably for systems containing the double-charged complex cations Mg^{2+}·CB7 [Figures 1(*b*), 2(*b*) (curves *5*), 1(*d*), and 2(*d*) (curves *6*)]. The data obtained for the system of single-charged complexes of CB$_n$ with alkali metal cations make it possible to conclude that the *C* values in this region are related to the free cavitand concentration ([CB$_n^{free}$]). This allows us, by comparing the results for the close systems, to use this effect for determining the stability constants of supramolecular cationic complexes for the cavitands under consideration.[8] In the particular case, the comparison of the data for the CB7 complexes with cations of different charges made it possible to draw only a qualitative conclusion on the lower stability of the complex cation Mg^{2+}·CB7 which meant the higher [CB7^{free}] concentration in the corresponding system. The difference in these values is the most pronounced when comparing the data for MgSO$_4$–CB7 and K$_2$SO$_4$–CB7, systems for the initial CB7 concentration of 10^{-5} mol dm^{-3}. As can be seen, under these conditions, irrespective of the potential scan direction, in the region more positive than the PZC, the larger differences are observed between *C vs. E* curves when compared with the initial CB7 concentration of 10^{-4} mol dm^{-3}, because the adsorption region in the K$_2$SO$_4$–CB7 system narrows down and the form of the

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‡ Under the conditions unfavorable for the MAdL formation (the highly stable cationic complex, the low CB$_n$ concentration), the adsorption region narrows down and its positive limit characterized by the stepwise variation in *C* finds itself at the more negative potential (*E* ~ −0.25 V) and determines the limit of the existence of the adsorption layer of cationic complexes on the electrode.[12]

corresponding *C* *vs.* *E* curve changes. This is due to a significant drop in [CB7^{free}] with a decrease in the initial concentration of CB7 by an order of magnitude. The value of [CB7^{free}] for the 0.1 M K$_2$SO$_4$ solution containing 10^{-5} mol dm^{-3} CB7 was assessed to be 2.7×10^{-7} mol dm^{-3} using the value of stability constant lg $K = 2.55$ for the complex K$^+$·CB7.[8] The found [CB7^{free}] is one order of magnitude lower than that found for the initial CB7 concentration of 10^{-4} mol dm^{-3}. For this reason, the MAdL is not formed in this solution and the overall picture of adsorption phenomena is determined solely by the complex K$^+$·CB7. It is the sharp, practically stepwise change in the electrode surface coverage by these complexes that is responsible for the corresponding characteristic changes in the form of the *C* *vs.* *E* curves.

As mentioned above, for $E \geqslant \sim 0.2$ V, the *C* *vs.* *E* curves measured at different *t* merge together. This effect manifests itself most clearly when the potential is scanned in the negative direction. As proposed earlier,[10] when analyzing the data for the MgSO$_4$–CB6 system, this effect can be explained by the fact that only free CB6 molecules are adsorbed at so high positive potentials (0.2–0.3 V). As the potential shifts to the higher negative values, *C* starts to depend on *t* at constant *E*, which at small *t* leads to the appearance of characteristic steps in *C* *vs.* *E* curves in the +0.2–0 V region which is explained by the slow formation of the MAdL. As previously,[10] we assume that the region in the *C* *vs.* *E* curve at the highest positive potentials (+0.3–0 V) and the lowest *t*, where this effect is minimum, can be used for determination of the adsorption parameters that in the first approximation can be attributed to the adsorption layer formed by CB7 molecules. The stability constant for the complex Mg^{2+}·CB7 is unknown; however, as was shown above, we can assume that this constant is close to lg $K = 2$ that assessed for Mg^{2+}·CB6.[10] Using this value, the [CB7^{free}] value in the 0.1 M MgSO$_4$ solution with addition of 10^{-4} mol dm^{-3} CB7 was found to be 10^{-5} mol dm^{-3}. Using the latter value, the parameters of the adsorption layer formed on the electrode in the potential interval from +0.3 to 0.0 V at *t* =3 s were calculated. The calculation was carried out using the proposed method[13] based on the regression analysis of adsorption data. In this case, we used the equations of the phenomenological theory of the reversible adsorption of organic compounds on electrodes based on the Frumkin isotherm:

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

where *B* is the adsorption equilibrium constant, *c* is the volume concentration of organic substance, θ is the surface coverage by organic substance, and *a* is the parameter characterizing the interaction between adsorbed particles. It was shown[14] that this isotherm is optimal for finding the parameters that characterize the properties of adsorption layers of organic compounds and allows 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 $\theta = 1$; and the parameter C_{m2}, which describes the variation of this quantity with potential. Parameters of the adsorption layer formed in the 0.1 M MgSO$_4$ solution containing 10^{-4} mol dm^{-3} CB7 ([CB7^{free}] = $= 10^{-5}$ mol dm^{-3}) calculated for the potential interval +0.3–0.0 V are as follows: $B_m = 10$ dm^3 mol^{-1}, $\Gamma_m \times 10^{10} = 0.44$ mol cm^{-2}, $-\Delta G_m = 34.7$ kJ mol^{-1}, $a_m = 0.32$, $C_m = 28.7$ μF cm^{-2}, $C_{m2} = = 22.9$ μF cm^{-2} V^{-2}, $\varphi_N = -0.04$ V, and $\Delta = 1.5$.
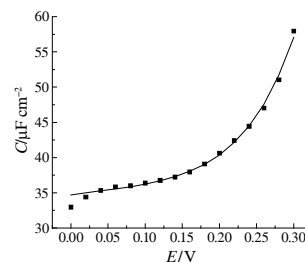

Figure 3 *C* *vs.* *E* curve for the 0.1 M MgSO$_4$ solution in the presence of 10^{-4} mol dm^{-3} CB7 obtained by scanning the potential in negative direction. The points refer to experimental data ($t = 3$ s) and the line was calculated with adsorption parameters obtained for the potential range from +0.3 to 0.0 V for [CB7^{free}] = 10^{-5} mol dm^{-3}.

The comparison of these results with those for the MgSO$_4$–CB6 system obtained under the same conditions reveals their principal closeness. The low φ_N values suggest the adsorption of neutral species, and the small values of the parameter *a* point to the weak attractive interaction between adsorbed species. Using these parameters, we calculated the *C* *vs.* *E* dependence for the potential region of +0.3–0 V. A comparison of the calculated *C* *vs.* *E* dependence with experimental data demonstrated their adequate agreement (Figure 3).

The presented results complement the emerging array of data, which analysis makes it possible to identify patterns in the formation of adsorption layers of supramolecular cationic complexes of cucurbiturils. Adsorption parameters were obtained for the adsorption layer formed in the MgSO$_4$–CB7 system at extremely high positive potentials and consisting almost entirely of CB7 molecules.

References

1 R. Behrend, E. Meyer and F. Rusche, *Justus Liebigs Ann. Chem.*, 1905, **339**, 1; https://doi.org/10.1002/jlac.19053390102.
2 W. A. Freeman, W. L. Mock and N.-Y. Shih, *J. Am. Chem. Soc.*, 1981, **103**, 7367; https://doi.org/10.1021/ja00414a070.
3 E. Masson, X. Ling, R. Joseph, L. Kyeremeh-Mensah and X. Lu, *RSC Adv.*, 2012, **2**, 1213; https://doi.org/10.1039/C1RA00768H.
4 K. I. Assaf and W. M. Nau, *Chem. Soc. Rev.*, 2015, **44**, 394; https://doi.org/10.1039/C4CS00273C.
5 K. Kim, N. Selvapalam, Y. H. Ko, K. M. Park, D. Kim and J. Kim, *Chem. Soc. Rev.*, 2007, **36**, 267; https://doi.org/10.1039/B603088M.
6 O. A. Gerasko, E. A. Kovalenko and V. P. Fedin, *Russ. Chem. Rev.*, 2016, **85**, 795; https://doi.org/10.1070/RCR4595.
7 B. C. M. A. Ashwin, P. Shanmugavelan and P. M. Mareeswaran, *J. Inclusion Phenom. Macrocyclic Chem.*, 2020, **98**, 149; https://doi.org/10.1007/s10847-020-01028-4.
8 E. V. Stenina and L. N. Sviridova, *Inorg. Chim. Acta*, 2023, **556**, 121653; https://doi.org/10.1016/j.ica.2023.121653.
9 E. V. Stenina and L. N. Sviridova, *Mendeleev Commun.*, 2023, **33**, 376; https://doi.org/10.1016/j.mencom.2023.04.025.
10 E. V. Stenina and L. N. Sviridova, *Mendeleev Commun.*, 2024, **34**, 591; https://doi.org/10.1016/j.mencom.2024.06.040.
11 X. Lu and E. Masson, *Langmuir*, 2011, **27**, 3051; https://doi.org/10.1021/la104729j.
12 E. V. Stenina and L. N. Sviridova, *Russ. J. Electrochem.*, 2022, **58**, 1020; https://doi.org/10.1134/S1023193522110106.
13 B. B. Damaskin, V. A. Safonov and O. A. Baturina, *Russ. J. Electrochem.*, 1997, **33**, 105; https://www.pleiades.online/cgi-perl/search.pl?type= abstract&name=elchem&number=2&year=97&page=105.
14 A. N. Frumkin and B. B. Damaskin, in *Modern Aspects of Electrochemistry*, 1964, vol. 3, pp. 149–223; https://books.google.com/books/about/Modern_Aspects_of_Electrochemistry.html?id=NkhCAQAAIAAJ&hl=en&output=html_text&redir_esc=y.