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ScienceDirect
Mendeleev Commun., 2023, **33**, 376–379

Mendeleev
Communications

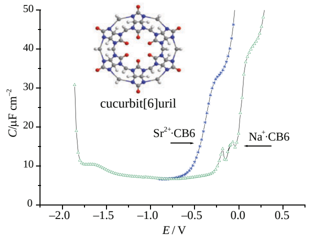
Features of adsorption phenomena in strontium salt solutions in the presence of some cavitands of cucurbituril family

Elena V. Stenina and Liana N. Sviridova*

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.
Fax: +7 495 939 0171; e-mail: slianan@mail.ru, estenina@yandex.ru

DOI: 10.1016/j.mencom.2023.04.025

The influence of the electrolyte nature and cation charge on the adsorption properties of cucurbit[6]uril supramolecular complexes are established and discussed. The results show the narrowing of the adsorption potential region of these complexes with increasing cation charge, and the possibility to form an adsorbate layer of supramolecular cations associated with surface-active electrolyte anions at the positive boundary of the adsorption potential region.



Influence of the complex cation charge and the nature of the anion

Keywords: supramolecular complexes, cucurbit[6]uril, cucurbit[7]uril, adsorption properties, $SrCl_2$ solutions.

Through the last years the attention of scientists was drawn to a new class of molecular cavitands of the cucurbituril CBn series (n is the number of glycoluril fragments that form the molecule). The first member of this homologous series was synthesized back in 1905;[1] however, the structure of these bulky molecules resembling pumpkins was determined only in 1981.[2] The unique combination of the properties of these compounds such as their rigid structure, large hydrophobic cavity, hydrophilic portals, ability to form complexes simultaneously with organic and inorganic species together with their stability in aggressive media, and low toxicity make them promising in various fields of chemistry and new technological applications.[3–8]

The behavior at interfaces is the least elaborated field of investigation of these cavitands. There are several publications on adsorption of certain cucurbiturils and their supramolecular complexes on gold, glass, and titanium oxide.[9,10] The only quantitative investigation of the adsorption properties of CBn complexes with certain organic compounds and alkali metal cations has been carried out on the model Hg electrode in our group.[11–15]

The present work is aimed at exploration of the adsorption phenomena at the interface between electrode and strontium salt solutions containing CB6 and CB7 with comparison of these data with those previously obtained for the CB7 + Na_2SO_4 system. The system $SrCl_2$ + CB6 was studied most thoroughly, and several results were obtained for the system $Sr(NO_3)_2$ + CB6. In the previous works we observed that the adsorption layers with different structures can be formed by CBn complexes with single-charged metal cations in an unusually wide potential region. It was shown that in the negative electrode surface charge region, an adsorbate layer is formed by supramolecular cations, whereas the transition to the positive charge region allows the formation of mixed adsorption layers which involve the cavitand molecules besides the supramolecular cations. It is evident that the character of electrostatic interactions taking part in the formation of such structures should undergo considerable changes with the variation of the electrode potential (charge). The transition from a negative to a positive charge of the electrode surface means a gradual transition from the attractive interaction of an adsorbed supramolecular cation with the electrode surface to the repulsive one. Naturally, the effect should be opposite for electrolyte anions. For free cavitand molecules, the transition to positive surface charges should also strengthen their electrostatic interaction with the electrode surface due to the presence of polarized carbonyl groups at portals. By and large, the transition to a positive electrode surface charge should weaken the electrostatic interaction of adsorbed supramolecular cations with the electrode surface and strengthen the effect of supporting electrolyte and free cavitands on the formation and properties of an adsorbed layer. In certain cases, this induces the formation of certain stable transition adsorption structures in the region more positive than the zero-charge potential.[11] Undoubtedly, as the charge of adsorbed supramolecular cationic complexes increases, these effects are expected to manifest themselves more clearly.

Figures 1 and 2 present the capacitance–potential (*C vs. E*) curves[†] which demonstrate how the adsorption phenomena in the system $SrCl_2$ + CB6 depend on cavitand concentration and time (t) of electrode exposure at each potential. Comparing the data in Figures 1 and 2 with the results obtained under similar conditions

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[†] The experiments were carried out on the electrode in the form of a hanging mercury drop by measuring the differential capacitance C as a function of the potential E by means of an Autolab potentiostat–galvanostat (Autolab/FRA, The Netherlands) at a 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 exposure at each potential t = 3–30 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 an inner diameter of 80 μm by means of a special tool supplied with the polarografic analyzer PA-3 (Czechoslovakia). The electrode potentials were measured and are given with respect to an AgCl electrode. Cucurbit[6]uril and cucurbit[7]uril (Fluka) were used without additional purification, $SrCl_2$ and $Sr(NO_3)_2$ were crystallized twice, Na_2SO_4 was crystallized twice and annealed at 500 °C, and water was purified on a Millipore unit. Solutions were deaerated with high purity argon.

(0.1 M electrolyte solution) for single-charged complexes $M^{+}\cdot$CB6[11] makes it possible to conclude that the dependence of *C* on cavitand concentration and time is weaker for the double-charged complexes $Sr^{2+}\cdot$CB6. Figure 3 illustrates how the potential region of adsorption of the $Sr^{2+}\cdot$CB6 complex depends on the $SrCl_2$ concentration. It is evident that an increase in the $SrCl_2$ concentration in the interval of 0.05–1 mol dm^{-3} makes the form of the *C vs. E* dependences more complicated in the vicinity of the positive limit of the adsorption region. In contrast to the system 10^{-2} M $SrCl_2$ + CB6, we observe the formation of steps approximately in the interval from −0.3 to −0.1 V at high electrolyte concentrations [Figures 3(*a*), 4(*a*)]. Moreover, the *C* value decreases with increasing $SrCl_2$ concentration in this potential interval (Figure 3). The observed effects make it possible to conclude that an increase in adsorption of Cl^- anions with increasing concentration in this potential region may result in the formation of an adsorption layer with a different structure involving these anions.

The analysis of these results compared with the *C vs. E* dependences in the systems $SrCl_2$ + CB6 and $Sr(NO_3)_2$ + CB6 (not shown) have demonstrated that the *C vs. E* dependences in these systems coincide at $E \leqslant -0.8$ V. This means that neither the surface-active Cl^- anions, nor the surface-inactive NO_3^- anions are adsorbed on the electrode surface. As one proceed to the positive potential region, the competition between Cl^- anions and $Sr^{2+}\cdot$CB6 complexes for adsorption sites is accompanied by an increase in the number of Cl^- anions adsorbed on the electrode surface[‡]. This leads to a gradual desorption of supramolecular cationic complexes and a corresponding increase in the *C* value. At the most positive potentials preceding the complete removal of these complexes from electrode surface, their electrostatic repulsion from the electrode and the competition with Cl^- anions may result in the appearance of a new adsorption layer structure

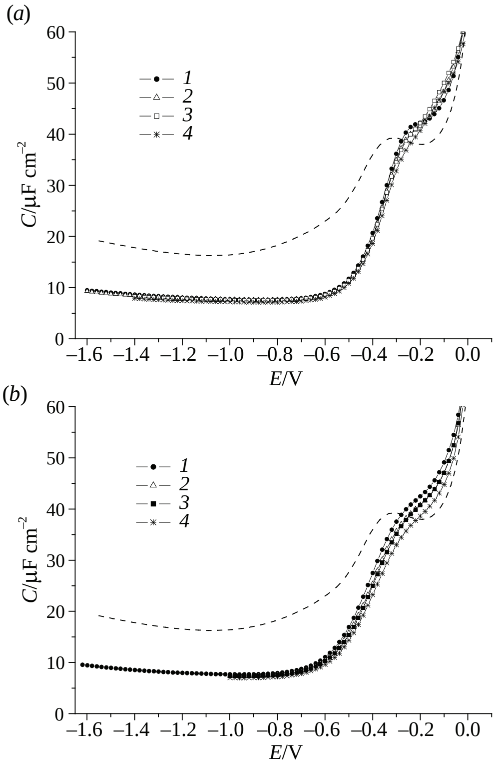

Figure 2 Experimental *C vs. E* curves in the 0.05 M $SrCl_2$ solution in the presence of 2.5×10^{-4} mol dm^{-3} CB6, obtained by potential scanning (*a*) from negative to positive and (*b*) from positive to negative *E* values. The electrode was held at every value of the potential for a period of: (*1*) 3, (*2*) 10, (*3*) 20, and (*4*) 30 s. Dashed lines are the *C vs. E* curves in the 0.05 M $SrCl_2$ solution.

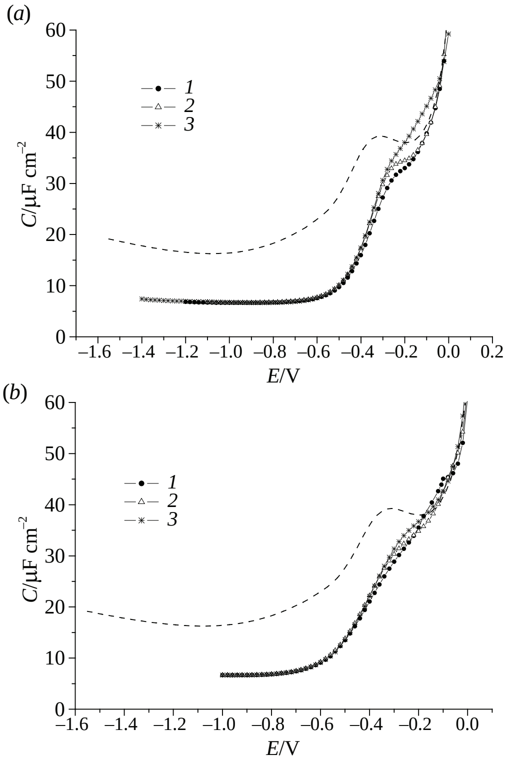

Figure 1 Experimental *C vs. E* curves in the 0.05 M $SrCl_2$ solution in the presence of CB6 in concentrations: (*1*) 5×10^{-5}, (*2*) 10^{-4}, (*3*) 2.5×10^{-4} mol dm^{-3}, obtained by potential scanning (*a*) from negative to positive and (*b*) from positive to negative *E* values for an electrode exposure time *t* = 30 s at each potential. Dashed lines are the *C vs. E* curves in the 0.05 M $SrCl_2$ solution.

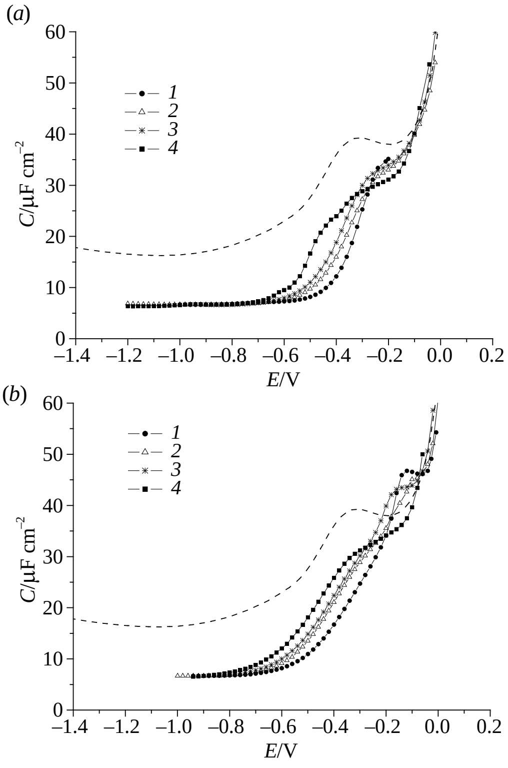

Figure 3 Experimental *C vs. E* curves in the 5×10^{-5} M CB6 solution in the presence of $SrCl_2$ in concentrations: (*1*) 10^{-2}, (*2*) 5×10^{-2} , (*3*) 10^{-1}, (*4*) 1 mol dm^{-3}, obtained by potential scanning (*a*) from negative to positive and (*b*) from positive to negative *E* values for a time of electrode exposure *t* = 30 s at each potential. Dashed lines are the *C vs. E* curves in the 0.05 M $SrCl_2$ solution.

[‡] Moreover, in the interval from −0.8 to −0.4 V the lower capacitance values are observed for the $SrCl_2$ + CB6 system as compared with the $Sr(NO_3)_2$ + CB6 system, which probably points to the involvement of Cl^- anions in the formation of a stronger adsorbate layer.

formed due to the electrostatic interaction of cationic complexes with Cl^- anions strongly adsorbed on the electrode. Probably, the bilayer structure Cl^-–$Sr^{2+}\cdot$CB6 is formed which is responsible for the appearance of the aforementioned steps in this potential region of the *C vs. E* dependences. The surface coverage by this adsorbate is sufficiently low, as follows from its estimates equal to 0.15–0.17. It is worth mentioning that when the potential is scanned in the negative direction where the supramolecular substances are adsorbed on the surface occupied with specifically adsorbed Cl^- anions, the structures described above can be formed only in 1 M $SrCl_2$ solutions where the surface coverage by these anions is maximal. It is probable that at lower $SrCl_2$ concentrations, the process is much slower under the same conditions.

Thus, the intricate form of the *C vs. E* dependences in the positive potential region for the $SrCl_2$ concentration lying in the interval of 0.05–1 mol dm^{-3} may be explained by the existence of two structures of the adsorption layer in this potential region. As the potential shifts to the positive direction, the initial region of ascending *C* (from about −0.7 to −0.3 V) corresponds to the desorption of the adsorbate layer consisting of $Sr^{2+}\cdot$CB6 complexes which were formed at more negative potentials, as a result of an increase in the positive electrode charge and also due to the increasing competition with Cl^- anions for adsorption sites. At more positive potentials (from about −0.3 to −0.1 V), a further increase in the positive electrode charge and, correspondingly, in the specific adsorption of Cl^- anions probably leads to the displacement of cationic complexes from their direct contact with the electrode surface and the formation of a certain bilayer structure of complex species bound to Cl^- anions specifically adsorbed on the electrode surface. In the 1 M $SrCl_2$ solution, in contrast to more dilute solutions, in the region where this structure forms we observe a stronger dependence on the electrode exposure time. In the system containing no surface-active anions (1 M Na_2SO_4 + CB7), no such time dependences were observed.[15]

For $SrCl_2$ concentrations in the range of 0.05–1 mol dm^{-3} the potential region of adsorption is virtually constant [Figure 3(*a*)]. It should be noted that at the first stage of desorption (from −0.7 to −0.3 V), when Cl^- anions begin to displace the cationic complexes, these systems are characterized by the shift of the *C vs. E* dependences to negative potentials. Thus, the potential region of the existence of the adsorbate layer formed by $Sr^{2+}\cdot$CB6 complexes on the electrode surface narrows; however, the region corresponding to the low surface coverage by these complexes strongly bound with the specifically adsorbed Cl^- ions widens. For the system 0.01 M $SrCl_2$ + CB6 [Figure 3(*a*)], the above step in the *C vs. E* dependences is absent and the adsorption region is narrower compared with more concentrated $SrCl_2$ solutions. This allows us to assume that in this system the only one kind of adsorbate typical of the initial stage of desorption of the layer of supramolecular cations is present.

Comparing the data regarding the effect of the electrolyte concentration on the adsorption of supramolecular cationic complexes $Sr^{2+}\cdot$CB6 in the $SrCl_2$ + CB6 system with the corresponding results for the Na_2SO_4 + CB7[15] system revealed the cardinal difference in the observed phenomena. For the single-charged supramolecular complexes at the 1 mol dm^{-3} electrolyte concentration, in the positive adsorption–desorption potential region we observed a sharp jump of the capacitance similar to that observed for the two-dimensional condensation of surface-active organic compounds.[16] This is associated with a sharp change in the electrode surface coverage by these complexes. At lower electrolyte concentrations, a wide potential region of adsorption–desorption of the mixed adsorption layer formed by supramolecular complexes and free cavitand molecules is observed. Moreover, the region of its adsorption considerably widens because its positive limit shifts farther in the positive direction. This comparison allows us to conclude that the interaction of double-charged supramolecular cationic complexes with the supporting electrolyte anions plays a more substantial role in the formation of adsorption layers by these complexes.

Thus, the analysis of results obtained for these systems makes it possible to conclude that the effect of the electrolyte concentration on the adsorption processes occurring in these systems may be opposite for surface-active and surface-inactive electrolytes. For the surface-inactive electrolyte (Na_2SO_4), an increase in its concentration narrows the region of adsorption for supramolecular cations due to the poorer conditions for the formation of mixed adsorption layer structures involving free cavitand molecules. On the contrary, for the surface-active electrolyte ($SrCl_2$), an increase in its concentration may even somewhat extend the adsorption region of these complexes which now form new adsorption structures with specifically adsorbed anions. The involvement of free cavitand species in these processes, even if occurs, is secondary.

It seemed interesting to compare how an increase in the charge of complex cations affects the potential region of their adsorption. Figure 4 shows the quite expected effect of the narrowing of the adsorption region upon transition from the single-charged cationic complex $Na^+\cdot$CB6 to the double-charged $Sr^{2+}\cdot$CB6. The positive limit of the potential region of adsorption for the $Sr^{2+}\cdot$CB6 complex is shifted by ~400 mV to the negative direction as compared with the $Na^+\cdot$CB6 complex, which is probably associated with stronger electrostatic repulsive forces. Undoubtedly, as was shown above, the analysis of this type should consider the effect of competitive adsorption of the supramolecular cation and the electrolyte anion. Apparently, for $Na^+\cdot$CB6, the above effect of the formation of a transition adsorbate structure is observed in the region of positive electrode charges when the potential is scanned from its negative values.

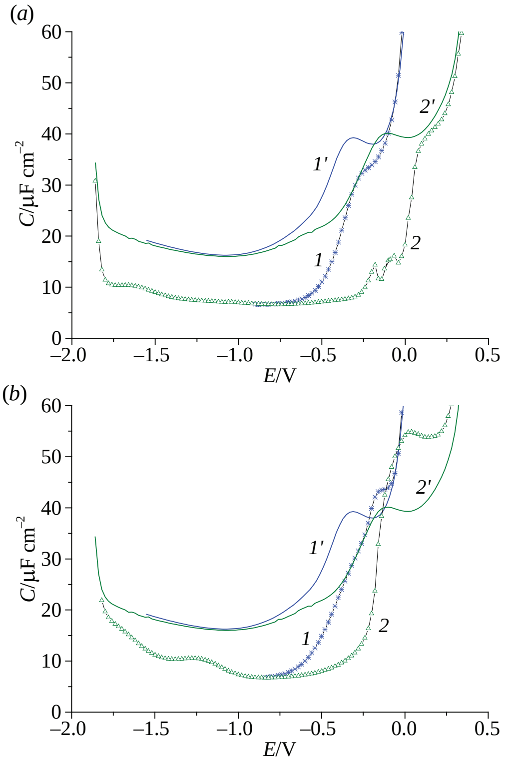

Figure 4 Experimental *C vs. E* curves in the 5 × 10^{-5} M CB6 solution in the presence of (*1*) 0.1 mol dm^{-3} $SrCl_2$ and (*2*) 0.1 mol dm^{-3} Na_2SO_4, obtained by potential scanning (*a*) from negative to positive and (*b*) from positive to negative *E* values for a time of electrode exposure at each potential t = 30 s. The *C vs. E* curves in (*1′*) 0.1 M $SrCl_2$ and (*2′*) 0.1 M Na_2SO_4 solutions.

This effect is typical of the most stable supramolecular cationic complexes. In particular, the complex $Na^+ \cdot CB6$ with the complex stability constant ($\lg K$) equal to 3.49 is the most stable among complexes of alkali metal cations with cavitand CB6. The stability constant for $Sr^{2+} \cdot CB6$ was found[17,18] to be $\lg K = 2.9$ (the comparison of the adsorption data for complexes $Sr^{2+} \cdot CB6$ and $Sr^{2+} \cdot CB7$ revealed the virtual coincidence of their stability constants). When the potential is scanned from its positive to negative values, the *C vs. E* dependences also considerably differ. It is quite probable that a much slower formation of the adsorption layer in the system $SrCl_2$ + CB6 may be associated with the competitive adsorption of the $Sr^{2+} \cdot CB6$ complex and the anion Cl^-.

The presented data are part of a systematic investigation of the adsorption behavior of cationic complexes containing molecular cavitands of the cucurbituril family at the electrode–solution interface. In the present work the effects originating from the nature of an electrolyte and a cation charge were identified and discussed. It was established that an increase in the cation charge leads to the narrowing of the adsorption potential region of these complexes and that the formation of an adsorbate layer of supramolecular cations associated with surface-active electrolyte anions is possible in the positive boundary of the adsorption potential region.

It is shown that the properties of adsorbate layers at the electrode–cavitand solution interface of the cucurbiturils series significantly depend on the nature of the inorganic electrolyte. The data obtained may be necessary for the interpretation of processes occurring on various surfaces (including electrodes) with immobilized layers of this type.

This work was supported by the M. V. Lomonosov Moscow State University Program of Development, grant no. AAAA-A21-121011590088-4.

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Received: 28th November 2022; Com. 22/7053