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Adsorption of an ammonium complex with cryptand 2.2.2 at the electrode/solution interface

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The adsorption behaviour of a complex formed by the ammonium cation with the macrobicyclic ligand cryptand 2.2.2 ([$NH_4^+ \subset$ 2.2.2]) at the electrode/solution interface was characterized as a function of electrode potential and the ligand concentration and quantitative parameters of the adsorbed layers of [$NH_4^+ \subset$ 2.2.2] were obtained.

Complexes with macropolycyclic ligands are of considerable current interest.[1–6] The electrochemical properties of cryptand 2.2.2 and its inclusion complexes with different cations and the surface activity of these cryptate complexes were described previously.[7–11] In this work, we studied the adsorption of ammonium cryptate ([$NH_4^+ \subset$ 2.2.2]) on a mercury electrode from 0.1 M NH_4Cl solutions containing different concentrations of cryptand 2.2.2. The stability constant of [$NH_4^+ \subset$ 2.2.2] is $\lg K_s = 4.5$.[12] The pH of these solutions was 8.2 (at this pH, ammonium cryptate occurs in a nonprotonated form).

Figure 1 shows the *C*–*E* relationships obtained in the test systems.† It can be seen that ammonium cryptate, as well as previously studied metal cryptates,[7–9] possess a very high surface activity at the mercury electrode/solution interface. This follows from a broad potential range where differential capacitance decreases regarding values for a supporting electrolyte as a result of ammonium cryptate adsorption. For example, at a complex concentration of 10^{-3} mol dm^{-3}, the extent of this range is ~1.5 V, and it decreases with reducing cryptand 2.2.2 concentration.

The scanning of potentials in the entire test range of potentials in opposite directions leads to a hysteresis effect at positive potentials. The potential of the middle adsorption region is near –0.9 V, and it corresponds to a maximal adsorption of [$NH_4^+ \subset$ 2.2.2]. This potential is more negative by 0.35 V than the zero charge electrode potential in the supporting electrolyte. Thus, the maximal adsorption of the complex [$NH_4^+ \subset$ 2.2.2] occurs at a negative charge of the electrode surface. This indicates that the charge of the included cation is screened incompletely.[1] Note that the maximal adsorption potential for neutral organic substances is close to the zero charge potential of the electrode in the supporting electrolyte.

† The studies were carried out on 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 25 mV. The *C vs. E* curves were recorded with times (*t* = 10–20 s) of the electrode exposure at each potential. These values of *t* are sufficiently large for adsorption equilibrium was established. The ideal polarizability interval of Hg electrode in the test system is –1.70 to –0.1 V. 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 diameters of 80 μm by a special tool included in a PA-3 polarographic analyzer. The electrode potentials were measured with respect to a saturated calomel electrode. Cryptand 2.2.2 (Merck) was used without additional purification; NH_4Cl was twice recrystallized; water was cleaned on a Millipor unit. Solutions were deaerated with high purity argon.

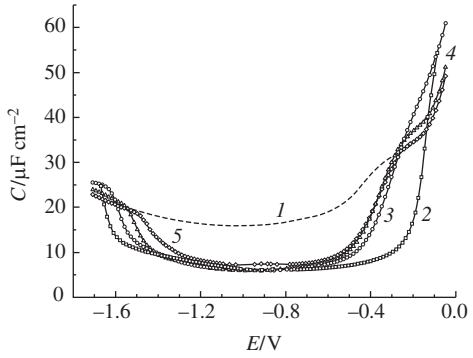

Figure 1 Experimental *C vs. E* curves of a Hg electrode in 0.1 M NH_4Cl solution (*1*) in the absence and (*2*)–(*5*) in the presence of cryptand 2.2.2 in concentrations of (*2*) 10^{-3}, (*3*) 10^{-4}, (*4*) 10^{-5} and (*5*) 10^{-6} mol dm^{-3}.

The experimental data were processed using regression analysis.[13] The adsorption parameters of [$NH_4^+ \subset$ 2.2.2] were calculated for the following three files of experimental *C*–*E* data in potential regions of (I) –1.7 to –0.2 V; (II) –1.7 to –0.9 V and (III) –0.9 to –0.2 V.

In the calculations, we used the following parameters: the maximum adsorption potential φ_m in the rational potential scale; the logarithm of the equilibrium constant of adsorption at a maximum 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 $\varphi = \varphi_m$; C_{m2}, the coefficient of the quadratic dependence of C_m on the potential; the parameter $A = RT\Gamma_m$, where Γ_m is the limiting surface concentration of the organic substance for $\theta = 1$, and *R* and *T* have their usual meanings. The parameter φ_N, which characterizes variations in the zero charge potential with the transition from $\theta = 0$ to $\theta = 1$, was found from the φ_m value.[13] The potential dependence of capacitance in the pure supporting electrolyte solution was described by an eigth-order polynomial.

The initial calculations of adsorption parameters carried out with the entire body of the experimental data led to a discrepancy between the calculated and experimental *C*–*E* curves. Because of this, the adsorption parameters were further obtained with the use of data corresponding to either negative or positive parts of the adsorption region (Table 1). These data testify that the test complex has a high surface activity (a large value of $\ln B_m$); it forms a closely packed adsorbed layer and essentially shifts the zero charge potential of the electrode to the positive values of *E*. The calculated parameters (in particular, the shift of the zero charge potential) are close to those for the complexes of alkali

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Table 1 Adsorption parameters for $[NH_4^+ \subset 2.2.2]$ at the mercury electrode interface with 0.1 M NH_4Cl.

Potential region	$-\varphi_m$/V	$\ln B_m$	A/μJ cm^{-2}	$\Gamma_m/10^{10}$ mol cm^{-2}	a_m	C_m/μF cm^{-2}	C_{m2}/μF cm^{-2} V^{-2}	φ_N/V	$\bar{\Delta}_i$ (%)
–1.7 to –0.2 V (I)	0.401	16.7	0.44	1.82	0.15	6.1	12.2	0.525	14.5
–1.7 to –0.9 V (II)	0.525	15.7	0.27	1.12	0.80	6.4	17.0	0.535	5.9
–0.9 to –0.2 V (III)	0.391	16.8	0.48	2.00	–0.22	6.1	15.4	0.611	17.3

metals with CR obtained previously.[7–9] The parameter a_m, which characterizes lateral interactions in the adsorbed layer, for the test complex is lower than that for cryptand 2.2.2 and its metal complexes. Probably, it points to a weaker interaction of the included NH_4^+ with the donor atoms of the ligand. This conclusion is supported by published data.[12]

Figure 2 shows the *C–E* relationships calculated with the use of the adsorption data of the complex corresponding to these two parts of the adsorption region. The experimental *C–E* curves and those calculated with use of the adsorption parameters corresponding to different adsorption regions (Table 1) are presented in Figure 3 for two cryptand 2.2.2 concentrations. A comparison between calculated and experimental *C–E* curves shows that experimental data for the negative part of the adsorption range are described with a greater accuracy. Thus, the properties of the adsorbed layer of ammonium cryptate change essentially with the potential and, correspondingly, the charge of the electrode surface. A more essential discrepancy between experimental and calculated dependences was observed at positive values of *E*. Probably, it depends on the fact that, in this potential region, the adsorption parameters are not constant. It means that a change in the electrode surface charge results in a progressive change in adsorption layer properties.

The relationship between the adsorption behaviour and the charge of an electrode surface for the cation complexes of cryptand 2.2.2 was established previously. Particularly, it is manifested for the diprotonated complex of cryptand 2.2.2, where a proton is localized on the external surface of the ligand at the nitrogen atom. Distinctions of adsorption behaviour of these complexes at different charges of electrode surface may be explained by their interaction with anions of supporting electrolyte. This interaction is displayed to the great extent at the positive charges of electrode surfaces. Probably, similar phenomena

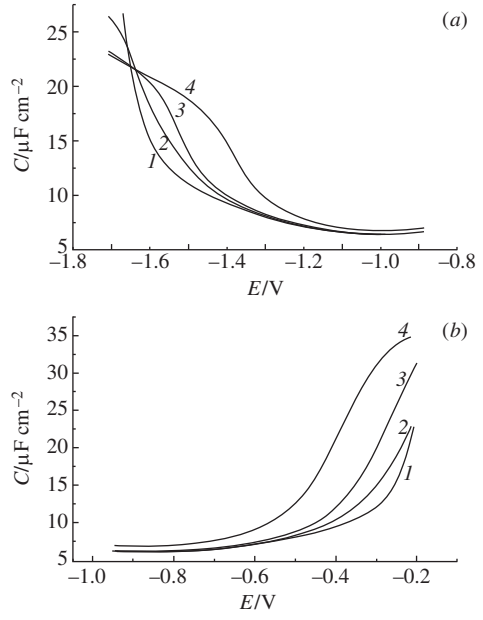

Figure 2 *C vs. E* curves of a Hg electrode in 0.1 M NH_4Cl solution in the presence of cryptand 2.2.2 in concentrations of (*1*) 10^{-3}, (*2*) 10^{-4}, (*3*) 10^{-5} and (*4*) 10^{-6} mol dm^{-3} calculated with adsorption parameters obtained for potential regions of (*a*) –1.7 to –0.9 V and (*b*) –0.9 to –0.2 V.

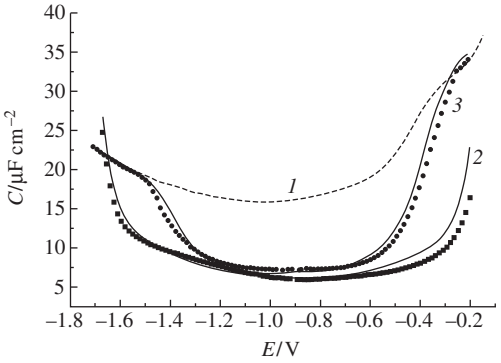

Figure 3 *C vs. E* curves of a Hg electrode in 0.1 M NH_4Cl solution (*1*) in the absence and (*2*), (*3*) in the presence of cryptand 2.2.2 in concentrations of (*2*) 10^{-3} and (*3*) 10^{-6} mol dm^{-3}. Points refer to experimental data, and lines refer to calculated data with adsorption parameters (see Table 1), obtained for potential regions of –1.7 to –0.9 and –0.9 to –0.2 V.

(and additional effect of the specific adsorption of Cl^- anions at more positive charges) take place in the case of the test complex. The interaction of $[NH_4^+ \subset 2.2.2]$ with anions is more intense, the more positive charge of electrode surface when there is excess of anions in the double electrical layer. The presence of anions in the adsorbed layer results in repulsion between species. It is evidenced by the negative values of a_m calculated with the use of the experimental data for the positive electrode surface charge. A shift of the electrode potential to negative values causes progressive decreasing of anions amount at the electrode surface. As a result, the interaction character of adsorbed species changes from repulsive to attractive. This phenomenon is reflected in the change of the sign of the parameter a_m from negative to positive under processing of data for the negative part of adsorption region. Thus, the conditions of the formation of $[NH_4^+ \subset 2.2.2]$ adsorbed layer change with the sign and value of electrode charge.

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