

# Self-inhibition phenomena in the electroreduction of hexamolybdocobaltate(III): A combined experimental and computational study

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## Abstract

Reduction of a heteropolyanion (HPA) of the Anderson type ( $[\text{CoMo}_6\text{O}_{24}\text{H}_6]^{3-}$ ) at a mercury electrode has been studied at different temperatures by using the polarographic technique. The results have been interpreted in terms of self-inhibition phenomena, which disclose non-monotonous dependence on the electrode charge. The adsorption interaction of the oxidized and reduced forms of HPA with the electrode surface was described in the framework of cluster model. The quantum chemical calculations were performed at the Density Functional Theory level. The distance-dependent electronic transmission coefficients were computed for three different orientations of  $[\text{CoMo}_6\text{O}_{24}\text{H}_6]^{3-}$  relative to the mercury surface. The planar orientation was found to be the least preferable from the viewpoint of both the adsorption energy and the orbital overlap. The experimental results have been explained qualitatively assuming the interplay between two orientations of the reduced form of HPA. The lateral interactions within the adlayer of anions (co-adsorbed with cations) were shown to be attractive and play an important role in self-inhibition.

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## 1. Introduction

Quantum-mechanical theory of electron transfer [1]<sup>1</sup> offers a challenge for molecular modeling level in the field of electrochemical kinetics (in particular, calculations of the innersphere reorganization [2], work terms [3], and electrode–reactant orbital overlap [4]). General

approach to the modeling of the rate constants and polarization curves [5,6] has germinated a new type of computational studies, which combine the calculation of model kinetic parameters with the construction of realistic models of the reaction layers. We believe that such a multilevel modeling which strongly rests on various computational approaches, not merely links theory and experiment, but also persuades some development of theory itself.

There are quite a few reactions for which the reaction layer can be presented by conducting sphere in the vicinity of metal plane, neglecting the molecular details of reactant and electrode/reactant interaction. A great deal

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of the electron transfer (ET) heterogeneous reactions are preceded, accompanied, or succeeded by specific adsorption, which experimental manifestations are rather diverse (from electrocatalysis to inhibition). In terms of the ET theory the adsorption affects simultaneously a number of key parameters. Along with some complications this special case provides a clear advantage, namely it weakens the uncertainty of the distance of closest approach, i.e. eliminates one of the main problems of constructing any model of the reaction layer. This paper presents a general approach to modeling the adsorption-complicated ET reactions; the hexamolybdocobaltate(III) heteropolyanion reduction on mercury is taken as example.

The electroreduction of heteropolyanions (HPA) was in the focus of numerous studies [7]. However, major attention was usually attracted to the reduction of oxometalate ligands, while only a few papers devoted to the reduction of central heteroatoms can be found [8–17]. The latter process can precede the reduction of the ligands if the oxidation state of heteroatom is high enough. One can expect, on the other hand, chemically reversible redox processes for transition metal heteroatoms stabilized in one and the same HPA structural type in both reduced and oxidized states. The surrounding of oxometalate can lead to relatively long distances of ET. As purely inorganic model reactants (molecular clusters) for studies of the long-range ET they provide an alternative to less stable metalloproteins.

Since the majority of transition metals tend to an octahedral coordination, the most favorable HPA type belongs to the so-called Anderson structure [18] (Keggin anions based on Co(II/III) and Cu(I/II) provide the same possibility, but the synthetic strategies are rather vague; other uniquely interesting reactants are Ce(III/IV)-based HPA [17]). An authoritative opinion [19] regarding the inability of the reduction of Anderson anions (based on experimental data [11]) should be rendered as a more particular statement: when ligands in these anions are reduced, no heteropolyblues are formed due to fast destructive chemical steps. This does not imply, however, the impossibility of heteroatom reduction. Recently we observed electrochemical processes of such type on mercury for  $\text{Na}_2\text{K}_6[\text{MnW}_6\text{O}_{24}]$  [15] and  $\text{Na}_3[\text{H}_6\text{Co(III)Mo}_6\text{O}_{24}]$  (which anion will be noted below as  $\text{CoMo}_6$ ) [16].

Dealing with the latter reactant we found striking barrier effects [20], which might result from the strong HPA adsorption on a mercury electrode [21,22]. These ‘self-inhibition’ effects are considered as an additional tool for understanding the peculiarities of the HPA adsorption on metals. A molecular level insight into the mechanism of such phenomena is a complicated and challenging problem. At the same time, computational chemistry methods and the cluster model of a metal surface can be very helpful to elucidate the interplay

between the electronic structure of HPA and their surface activity. The electronic structure of certain HPA of the Keggin, Wells-Dawson and Lindquist types [19] has been addressed earlier at different quantum chemical levels: INDO [23], DV- $X\alpha$  [24], ab initio SCF and DFT [25,26] (see also reviews [27,28]). It should be noted that no quantum chemical calculations were performed so far to model the Anderson-type HPA.

This paper is organized as follows. Some experimental details are reported in Section 2 with subsequent discussion of main results in Section 3. Details of quantum chemical calculations and the cluster model are briefly described in Section 4. The results of quantum chemical modeling are discussed in Section 5. The main qualitative predictions of model calculations are interfaced with experimental data in Section 6.

## 2. Experimental details

Currents were measured on a dropping mercury electrode (flow rate  $0.65 \text{ mg s}^{-1}$ , open circuit drop life 10.1 s) at various times (oscillographic registration in the course of the drop life time). For details of the polarographic setup see [15,17]. The potential  $E$  is given in respect to the saturated calomel electrode (SCE). The minimal observable current was equal to ca. 5 nA. For the supporting electrolyte a 0.5 M acetate buffer solution (pH 4.7) was used.

The  $\text{Na}_3[\text{H}_6\text{Co(III)Mo}_6\text{O}_{24}]$  reactant, and also  $\text{Na}_4[\text{H}_6\text{Co(II)Mo}_6\text{O}_{24}]$ , have been synthesized according to conventional techniques [19] and were recrystallized from bidistilled water. To estimate the equilibrium potential  $E^0$  for Co(II/III) in  $\text{CoMo}_6$ , we measured the cyclic voltammograms (CV) on a Pt electrode in solution containing equal quantities of oxidized Co(III)- and reduced Co(II)-containing species (ca. 0.2 mM each). Higher concentrations are unachievable for the low soluble reduced form. The oxidized form demonstrates higher solubility, which, however, was not enough for more direct potentiometric titration because the potential of the indicator electrode remained mixed. The peak separation was ca. 0.1 V and the voltammogram had a shape typical for quasireversible processes. We consider the value of  $E^0 \sim 0.2 \pm 0.1 \text{ V}$  as an estimate of the standard potential ( $E^0$ ).

## 3. Experimental manifestation of self-inhibition and phenomenological treatment

We were able to observe the  $\text{CoMo}_6$  reduction (cathodic current exceeding the background charging current) starting from 0.05 V. This value does not differ much from the above mentioned  $E^0$  value. The

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