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Inorganic barrier layers: electron transfer on mercury modified by tungstate

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Strong inhibition of anion reduction on a mercury electrode by adsorbed tungstate, WO_4^{2-}, and dodecatungstate, $[H_2W_{12}O_{42}]^{10-}$, was found and considered as surface blocking with solid-like tungstate adlayers.

Long-distance electron transfer (ET) through barrier layers became a topic of intensive studies during the last decade as it is intended to contribute to molecular and biomolecular electronics. Along with traditional organic spacers,[1,2] alkanethiols,[3] steroids[4] and lipid derivatives[5] are actively used, whereas the examples of inorganic spacers are practically absent. Inorganic 2D-films based on tungstates and polytungstates, which are quite stable at high positive electrode free charges, demonstrate complete monolayer coverages on positively charged mercury at negligible bulk concentrations.[6–8] These systems with pronounced lateral interactions resulting from the coadsorption of multi-charged anions with supporting cations, are good candidates to supplement or, in some cases, serve in place of other barrier systems. Their ability to inhibit the electrode reactions of anions on mercury is demonstrated in this communication.

Currents were measured on a dropping mercury electrode (flow rate of 0.65 mg s^{-1} and open circuit drop life of 10.1 s) at the end of the drop life time.[8] Potential E is given with respect to SCE. The minimal observable current was approximately equal to 5 nA. The supporting electrolyte was a 0.5 M acetate buffer solution (pH 4.7). All reactants were recrystallised from bidistilled water. Model reactions were represented by the electroreduction of $S_2O_8^{2-}$, BrO_4^-, $PtCl_4^{2-}$, $[Co(EDTA)]^-$ and 1-nitro-3,6,8-trisulfonaphthalic acid.

A tungstate-containing supporting electrolyte demonstrated no current response up to E of –0.8 to –0.9 V (curves *2* and *3* in Figure 1); catalytic hydrogen evolution conjugated (or, probably, coupled) with tungstate reduction is believed to start at more positive potentials.

Peroxodisulfate reduction on DME in an acetate buffer medium proceeded under diffusion limitations up to $E \approx -1.1$ V; at more negative potentials, proton discharge contribution became significant (curve *1* in Figure 1). A polarographic maximum was observed at potentials more positive than –0.3 V in tungstate-free solutions.[9] In the presence of submillimolar amounts of tungstates, this maximum was completely suppressed. Moreover, the reduction started only at potentials more positive than 0 and –0.15 V in the presence of WO_4^{2-} and $[H_2W_{12}O_{42}]^{10-}$, respectively (curves *4–7* in Figure 1). The reduction wave shifts towards more negative potentials with concentration of the additive (curves *5–7* in Figure 1). The slopes of these waves are close to 0.06 V, in formal agreement with the behaviour of quasi-reversible electron-transfer processes. However, currents below the limiting current demonstrate their preferentially kinetic origin as being independent of the height of an Hg column. The limiting diffusion current is not affected by tungstates. This fact gives evidence for a rather small size of tungstate islands (if any) as compared with the thickness of a diffusion layer. In the opposite case, one should expect a pronounced decrease of the limiting diffusion current, like that on a 'partly puttyed electrode'.

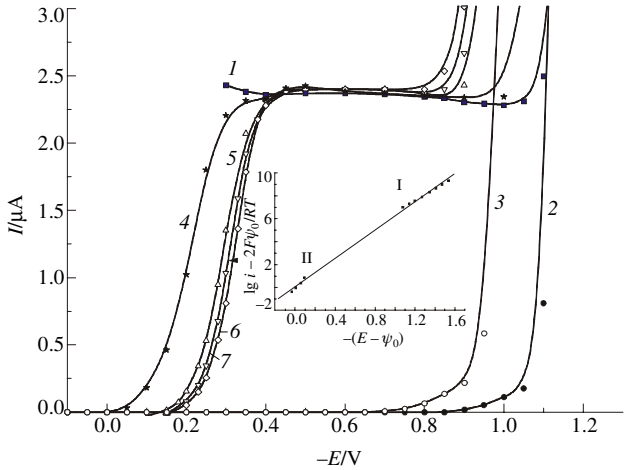

Figure 1 Polarograms of reduction measured on a dropping mercury electrode in a 0.5 M acetate buffer solution (pH 4.7) in the presence of (*1*) 10^{-3} N $K_2S_2O_8$, (*2*) 5×10^{-3} M Na_2WO_4, (*3*) 2×10^{-4} M $Na_{10}[H_2W_{12}O_{42}]$, (*4*) 10^{-3} N $K_2S_2O_8$ with the addition of 2×10^{-4} M $Na_{10}[H_2W_{12}O_{42}]$, (*5*)–(*7*) or Na_2WO_4, *x*M, *x*: (*5*) 2×10^{-4}, (*6*) 5×10^{-4}, (*7*) 1×10^{-3}. Insert presents the corrected Tafel plot which right part (I) is taken from ref. 9, and the left part is recalculated from curves (*5*)–(*7*) using the values of ψ_0 (potential of an outer Helmholtz plane for 0.5 M 1,1-electrolyte[11]).

The strong inhibition of $S_2O_8^{2-}$ electroreduction by inorganic additives was observed earlier only for halide additives[10] in essentially higher (molar) concentrations. The observed phenomenon was interpreted in terms of electrostatic effects without assumptions on surface blocking. The suppression of polarographic maximum in the presence of centimolar halide amounts was still incomplete.[10]

The strong inhibition of perbromate reduction was also observed with both tungstate and dodecatungstate (Figure 2). Note that there is no effect of solution pH in the region of pH 2–5, in spite of the pronounced pH dependence of BrO_4^- reduction kinetics in tungstate-free solutions.[4] Apparently, the current in the region of tungstate adsorption is determined only by pH-independent surface coverage by the adsorbate under study.

In order to clarify the factors affecting the inhibition by tungstates, we also checked the effect of dodecatungstate on other electrode processes.

For single-electron $[Co^{III}EDTA]^-$ reduction, the inhibition by dodecatungstate with a vanishingly small current at $E > -0.15$ V was observed. At $E < -0.4$ V, currents were equal in the absence and in the presence of dodecatungstate. One can conclude similar inhibition of $[Co^{III}EDTA]^-$ and $S_2O_8^{2-}$, in spite of a pronounced difference of overvoltages (> 2 V) and, correspondingly, formal rate constants of these processes at a given potential .

The multi-electron pH-dependent reduction of 1-nitro-3,6,8-trisulfonaphthalic acid, which is assumed to be complicated by a number of chemical steps, starts just at the potentials of partial tungstate desorption.[8] Correspondingly, the inhibition was found to be less pronounced than that for other reactants. Note that a weakly pronounced maximum at $E = 0.5$–0.6 V was suppressed by tungstate.

The complete suppression of a polarographic maximum and a shift of the reduction wave towards more negative potentials also took place for tetrachloroplatinite reduction in freshly prepared non-hydrolysed solutions (Figure 3). Limiting diffusion current was observed in the region from –0.3 to –0.8 V, with a small but well-reproducible pit in the vicinity of pzc (–0.5 V). The nature of this feature remains unclear. Limiting current value corresponds to the transfer of two electrons. Hence, we can conclude that in the absence and in the presence of tungstate the reduction of Pt^{II} to Pt metal takes place. We should stress that for $PtCl_4^{2-}$, like $S_2O_8^{2-}$, reduction on mercury proceeds at extremely high overvoltages (> 2 V) in this potential region. At

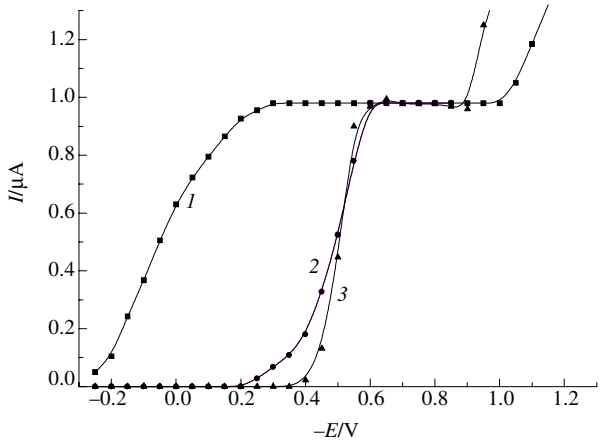

Figure 2 Polarograms of reduction measured on a dropping mercury electrode in a 0.5 M acetate buffer solution (pH 4.7) in the presence of (*1*) 2×10^{-4} N $LiBrO_4$, (*2*) with addition of 5×10^{-4} M Na_2WO_4 and (*3*) with addition of 5×10^{-4} M $Na_{10}[H_2W_{12}O_{42}]$.

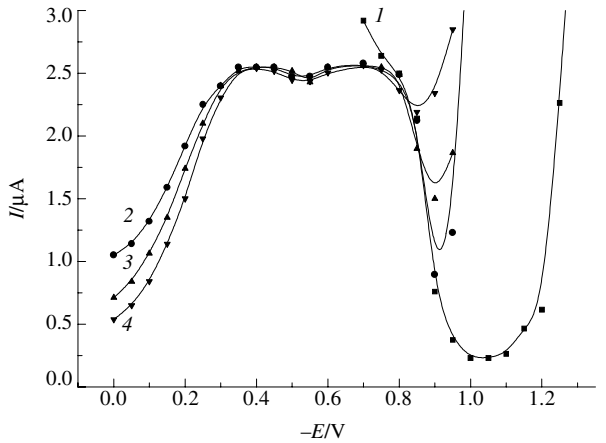

Figure 3 Polarograms of reduction measured on a dropping mercury electrode in a 0.5 M acetate buffer solution (pH 4.7) in the presence of 5×10^{-4} M K_2PtCl_4 with additions of *x*M $Na_{10}[H_2W_{12}O_{42}]$, *x*: (*1*) 0, (*2*) 2×10^{-4}, (*3*) 5×10^{-4}, (*4*) 1×10^{-3}.

high negative electrode charges, inhibition is masked by catalytic hydrogen evolution from tungstates.

Comparing the above reactions, we can conclude that at least two factors can be, in general, responsible for the degree of inhibition: the competitive specific adsorption of reacting anions (and/or reaction products) and tungstates, and the formal rate constant of a certain reaction at a given potential.

The equilibrium adsorption values (Γ) for tungstate can be estimated from surface tension data.[8] The portions of a free mercury surface can be estimated from these Γ values under assumption that the highest observed value ($\Gamma_{max} = 4\times10^{-10}$ mol cm^{-2}) corresponds to complete monolayer (the corresponding square per adsorbed anion equals 0.42 nm^2, the value is close to the molecular size for solid tungstates). Note that the $(1 - \Gamma/\Gamma_{max})$ *vs. E* plot copies the general shape of waves (curves *5–7* in Figure 1), especially in the region of low current densities where a mass transport contribution is minor. Hence, the shape of waves in Figure 1 can be explained by the potential-dependent degree of blocking rather than by a usual behaviour of quasi-reversible electrode reactions.

We used $(1 - \Gamma/\Gamma_{max})$ values for rebuilding data of Figure 1 under an assumption that the $S_2O_8^{2-}$ reduction occurs only on the free mercury surface, and ET *via* tungstate makes no contribution. According to Lipkowski *et al.*,[2] this model corresponds to a solid-like 2D tungstate film. The resulting values of currents (after correction for a mass transport contribution) demonstrated minor dependence on WO_4^{2-} concentration, in general agreement with the solid-like film model.

Hence, as a rough approximation, non-zero currents observed in our experiments correspond preferentially to ET on the free electrode surface, and the difference of currents in the presence and absence of tungstates can be considered as a measure of tungstate adsorption.

We applied a traditional procedure of constructing so-called corrected Tafel plots (CTP), which means plotting the values of current corrected for electrostatic repulsion/attraction.[9,11] The model parameter used for this treatment is the potential of an outer Helmholtz plane (ψ_0) (correspondingly, a work term for doubly-charged reactant is $2F\psi_0$, the difference of reactant and product work terms is $F\psi_0$). As we are dealing with concentrated solutions, the values of ψ_0 do not exceed few dozens of mV,[11] and the accuracy of their determination gives a minor contribution. The insert in Figure 1 demonstrates that two regions of CTP (region I for negative electrode charges[7] and region II plotted on the basis of curves *5–7*, Figure 1) find themselves, under the first approximation, at one and the same straight line. This is a surprising fact, which can be qualitatively interpreted in terms of the very low specific adsorption of a reactant and the screening of its repulsion by adsorbed tungstate anions due to the presence of coadsorbed cations. However, we cannot exclude a sort of compensation (both effects give comparable contributions of opposite signs).

The formal transfer coefficient estimated from the slope of this line equals 0.33±0.05, *i.e.*, is close to the published value.[9] One can conclude from this fact that the structure of the reaction layer escapes a pronounced charge-induced reconstruction when going from region I to region II. In the opposite case (if the localization of a reactant is charge-dependent due to peroxodisulfate adsorption on positively charged mercury, and electrostatic interaction plays a secondary role in the work term value for region II), one should expect a pronounced shift of region II towards higher values of corrected current.

The preliminary characterisation of tungstate barrier properties presented above clarifies several general features. First of all, in the presence of a close-packed tungstate layer, the ET rate decreases by at least four or five orders of magnitude. A more exact value can be obtained in the future from the measurements of currents below 5 nA. The cathodic limit of a strong inhibition region seems to depend on the ability of a reactant to coadsorb with tungstate, namely, this limit is more negative, the stronger their adsorption ability. On the other hand, in the region of potentials, in which the layers are incomplete but the coverages are still high, ET takes place on the unoccupied electrode surface, most probably, at the isolated sites with molecular dimensions, and there is no evidence for a pronounced decrease of the rate constant per unoccupied surface area in comparison with this value in a tungstate-free solution, as was shown above for peroxodisulfate reduction. This provides a sensitive instrument to determine quantitatively a surface excess from kinetic data.

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