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# Cognitive Aspects of the Cap-Pair Effect[*]

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The paper discusses the cap-pair rule discovered by the authors. The cap-pair rule is associated with acceleration of electrode processes by organic substances. The mechanism and the kinetics of electrode processes in aqueous solutions and aqueous-organic solvents are discussed. A new concept of the "piloting ion" to study mixed adsorption layers based on the cap-pair rule is presented.

**Key words**: catalytic-activity, rate constant, mixed solvents, mixed adsorption layers

The evaluation of the mechanism and the kinetics of electrode processes has always been one of the fundamental and practically important problems in electrochemistry. For many years the influence of organic substances on the course of electrode processes was associated with their inhibitory character [1–10]. In this paper we present the study of the accelerating action of organic substances on electroreduction occurring on the mercury electrode. Vast experimental material regarding the catalytic action of over 100 organic substances on Zn(II), Cd(II), Bi(III) and In(III) ions electroreduction allowed to formulate the cap-pair rule [11–13] determining the conditions which must be satisfied by the depolarizer and the supporting electrolyte – organic substance system to accelerate the electrode process.

These conditions are:

- polarographically inactive organic substance must contain either sulfur or nitrogen atoms with free electron pairs able to form coordination bonds with the depolarizer ions,
- in the range of the depolarizer reduction potential the organic substance must be connected with the mercury electrode surface in a labile way.

The accelerating effect of organic substances on the electroreduction of metal ions can be compared with the catalytic action of halide ions. The interactions between metal ions and the specifically adsorbed halide ions are described by some theoretical models of which one can distinguish:

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[*] Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

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- anion bridging models which postulate the presence of an additional stage of the process *i.e.* a chemical reaction between the depolarizer and the specifically adsorbed anions [14–17];
- electrostatic models associating the change of the reaction rate with the electrostatic interaction between the active complex and the specifically adsorbed anions [18–24].

These models complement one another in the description of the same process.

The papers published in 1984 and 1986 by Ikeda [25] and Souto *et al*. [26] discussed the catalytic action of organic substances on electrode processes. Over 100 papers as well as doctoral and habilitation dissertations published in 1978–2003 dealt with the mechanism of the cap-pair effect in aqueous solutions and water-organic solvents. These papers also presented plausible applications for the cap-pair effect, *e.g.* the studies of the composition and structure of the mixed adsorption layers or the resolution of various analytical problems.

## RESULTS AND DISCUSSION

**Mechanism of the cap-pair effect in aqueous solutions**. For the study of the mechanism of the cap-pair effect the quasireversible reducible depolarizers: Zn(II), Bi(III) and In(III) were used. Polarography, chronovoltammetry, chronocoulometry and the impedance method were used as the major experimental techniques.

The reduction of the mentioned depolarizers is a multi-stage process, during which the metal atoms are transferred to the mercury phase and the amalgam is formed. It has been established elsewhere, that the limiting current of the electroreduction of Zn(II) ions [27–31] and Bi(III) ions [32] in the presence of catalytic substances does not change. This suggests, that the adsorbed catalytic substances instead of blocking the surface increase its activity. The dependence of the limiting current on the height of mercury reservoir indicates diffusive [27–32] or kinetic [33] control of the process.

The constancy of the half-wave potential of ion electroreduction in the presence of catalytic substances indicates that no stable complexes of depolarizer ions with the catalyst molecules are formed in the bulk solution. The lack of those complexes was additionally confirmed by the spectrophotometric experiments.

The acceleration of the electrode processes caused only by those organic reagents which have free electron pairs suggests that the depolarizer-catalytic substance complexes were formed. The latter reaction occurred preferentially on the electrode surface because of significant local catalyst concentration resulting from its adsorption on the mercury electrode. The adsorption of the organics proceeded with the partial dislocation of charge. The catalytic substance adsorption on the electrode surface advantageously shifted the equilibrium of the complex creation. The dependence of the standard rate constants of metal ions electroreduction on the surface excess of the catalytic substance for the studied systems was rectilinear. According to Tamamushi

[34] the latter could be the evidence of complex formation. The deviations from linearity were observed at higher surface excess values [32]. These deviations seemed to result from the changes of catalyst molecule orientation on the surface of the electrode [35].

The studies of catalytic activity of 2,4-; 2,6- and 3,4-diaminotoluene isomers [29,31,36] on the electrochemical reduction of Zn(II) ions indicated that the differences in catalytic activity of these isomers mainly resulted from their complex formation properties. Table 1 presents the values of the individual standard rate constants of Zn(II) electroreduction at various concentrations of diaminotoluene isomers studied. It seems that the presence of the ortho positioned amine groups in 3,4-diaminotoluene generated optimal conditions for the formation of stable complex connections, whereas no significant differences in the adsorption of the studied isomers on the mercury electrode were observed.

**Table 1.** Values of the corrected individual rate constants of the electroreduction of Zn(II) ions extrapolated to the $E_f^0$ and surface excesses at the $E_f^0$ in 1 M $NaClO_4$ solutions at various concentrations of isomers of diaminotoluene [31].

| $c\ 10^3$ [M] | $\Gamma\ 10^{10}$ [mol cm$^{-2}$] | $k_{s1}^t 10^3$ [cm s$^{-1}$] | $k_{s2}^t\ 10^2$ [cm s$^{-1}$] |
|---|---|---|---|
| 0 | – | 0.97 | 5.00 |
| 3,4 DAT | | | |
| 1 | 0.35 | 5.98 | 0.55 |
| 2 | 0.82 | 7.30 | 0.69 |
| 5 | 2.25 | 19.06 | 1.55 |
| 2,4 DAT | | | |
| 1 | 0.43 | 1.80 | 0.55 |
| 2 | 1.10 | 2.07 | 0.92 |
| 5 | 2.05 | 3.70 | 1.06 |
| 10 | 2.97 | 5.52 | 1.16 |
| 20 | 3.50 | 6.60 | 1.69 |
| 2,6 DAT | | | |
| 1 | 0.56 | 0.81 | 2.07 |
| 2 | 1.03 | 0.97 | 2.26 |
| 5 | 1.61 | 1.13 | 2.44 |
| 10 | 2.11 | 1.18 | 2.67 |
| 20 | 2.55 | 1.43 | 2.78 |

In addition the catalytic activity is evidenced in the cyclic chronovoltammetry experimental results (Fig. 1). The increase of catalyst concentration in the solution caused the increase of peak height and the decrease of the cathodic and anodic peak separation ($\Delta E_{ca}$) [33]. The shape of the cyclic curve indicated that the process is controlled by the rate of the preceding reaction [37]. The insignificant influence of the polarization rate on the $\Delta E_{ca}$ (Fig. 2) indicated that the step controlling the overall reaction rate is a chemical one.

The catalytic behavior of organic substances must be connected with their ability to remove molecules of coordinated water from the inner hydration shell. The introduction of the foreign ligand (such as an organic molecule) into the coordination sphere of an aquo-ion accelerates the displacement of the remaining water molecules.

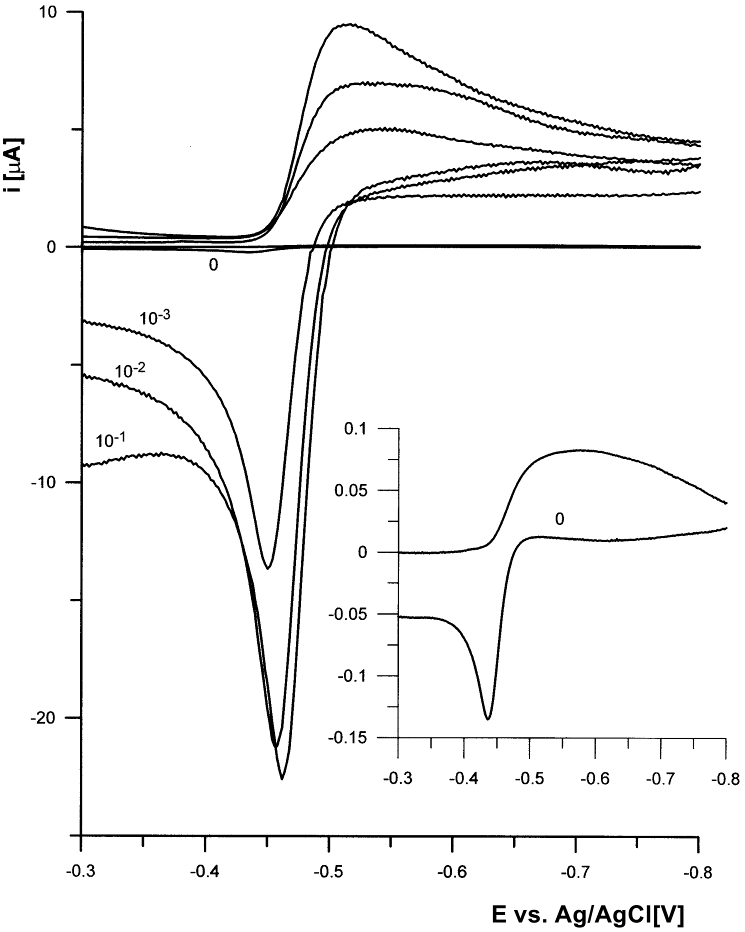

**Figure 1.** Cyclic voltammogram of $10^{-3}$ M In(III) in $HClO_4$ pH 1 + TU. Concentration of TU (M) indicated for each curve. Scan rate 50 mV $s^{-1}$, f = 120 Hz, ΔE = 20 mV.

Hence labilization of the hydration sphere plays a key role in all ligand catalyzed reductions of metal ions [38].

In order to establish if the depolarizer ions can be accumulated in the surface layer by the interaction with the adsorbed catalyst, chronocoulometric measurements were made. The double layer charge recorded in the blank solution was subtracted from the key experimental results. The corrected values of the maximal charge of depolarizer electroreduction were plotted against the integration time. The acquired relations were always linear and intersected the origin at all times. The latter indicates that the induced adsorption of the depolarizer ions cannot be detected within the limits of the experimental error [29,30,32,36,39]. The ln $k_f^t$ = f(E) relations (where $k_f^t$ is the true rate constant) obtained from the impedance measurements were not linear and the slope of the curves changed with both the potential value and the catalyst concentra-

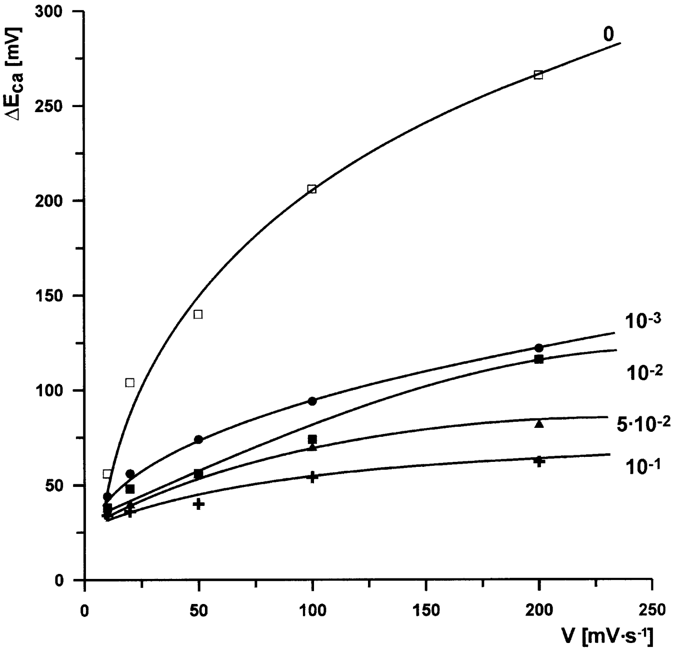

**Figure 2.** Influence of the polarization rate on the difference between potentials of cathodic and anodic peaks for the In(III)/In(Hg) couple in $HClO_4$ pH 1 + TU. Concentration of TU (M) indicated for each curve.

tion (Fig. 3). This curvature can be explained if the successive electron transfer is presumed. The accelerating effect is larger at more negative potentials and it seems to be absent in the most positive potential region. If we suppose, that the charge transfer proceeds *via* consecutive single electron transfer steps, then at the most negative potentials the first electron transfer is rate determining. The relations presented in Fig. 3 clearly show that the influence of catalyst on the rate of the first electron transfer is greater than its impact on the overall rate constants [29–33,39].

The corrected individual rate constants of the electroreduction of Zn(II) ions at various catalyst concentrations were determined. The rate constants of the first electron transfer increased with the increasing concentration of all catalytic substances. The transfer of the second electron was inhibited at the lowest studied concentrations of catalytic substances and then increased with the increasing concentration [29–31,39]. The second electron transfer largely depends on the double layer effects like the orientation of molecules on the electrode surface [39]. The active complexes probably participate in the transfer of consecutive electrons. It seems that the composition of these complexes is diversified. The latter is in agreement with the Marcus theory, which predicts the change of ion sheath after partial loss of charge. The rate of the last electron transfer is also associated with the availability of the electrode surface – a very important aspect of amalgams formation. Electrocatalysis is a result of the parallel reactions of stepwise complex formation. A process in which the simple

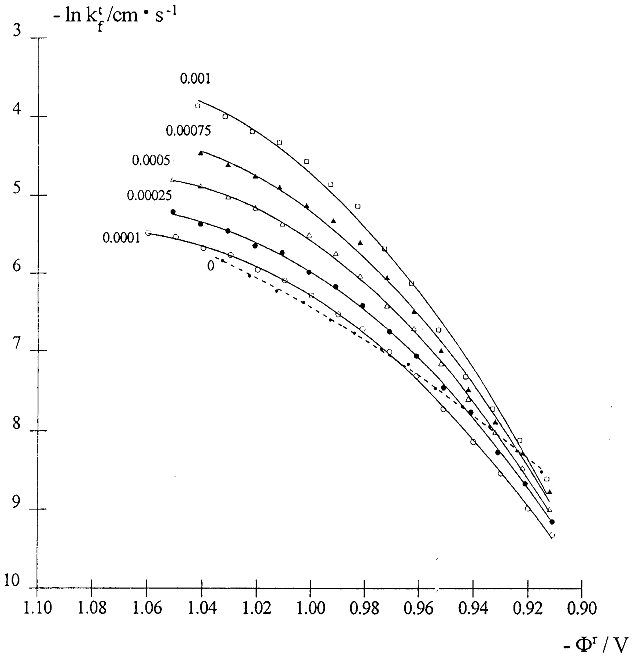

**Figure 3.** The natural logarithms of the corrected rate constants *versus* the potential in the reaction plane for the Zn(II)/Zn(Hg) system in 1 M $NaClO_4$ + 0.001 M $HClO_4$ at various N,N′-di-isopropylthiourea concentrations (M) indicated for each curve.

and the complex bulk ions with the ligand-catalyst and the electrode adsorbed ligand-catalyst participate. The ligand-catalysts are regenerated by the reduction of the electroactive complex [40,41].

The formation of the coordination bond in a ligand-induced adsorption is distinguished from the coordination bond in the directly adsorbed complex. As Mark [42] noted, for general adsorption of complexes, the latter should result in a general labilization of the inner coordination sphere of the complex and according to Heyrovsky's concept it should cause a bridge effect in the electron transfer.

**Mechanism of cap-pair effect in aqueous-organic solvents**. The theories formulated for aqueous solutions must be experimentally verified for other solvents. However, the poor solubility and instability of some substances in aqueous media makes it impossible to investigate them in the water containing environment. The use of non-aqueous solvents makes the study of water insoluble or water unstable substances possible. The non-aqueous electrolytes can also be useful when the range of potentials available in aqueous solutions is too narrow. The rate and the course of electrode process may as well be affected by the change of solutions' composition.

To evaluate if the acceleration of electrode processes on the mercury electrode takes place in aqueous solutions only [11–13], the studies on electrode process acceleration by organic compounds in water-organic solvents were carried out. These studies included the determination of the relation between the electrode kinetics and the following parameters: solvent composition, accelerating substances' relative surface excess and accelerating substances' concentration.

The studies were performed in mixed aqueous-organic solvents: water + methanol (MeOH) [43–46], water + ethanol (EtOH) [46,47–51], water + acetone (AC) [49], water + dimethyl sulfoxide (DMSO) [44,52–54] and water + N,N-dimethylformamide (DMF) [55,44] which differ in solvating properties in relation to Zn(II) ions. Thiourea (TU) [43,48,50,52,53,55], thiourea derivatives [50,51], aminobenzoic acid isomers [45] and p-toluidine [56] were used as the accelerating agents. These substances satisfied the conditions of the cap-pair effect occurrence in aqueous solutions.

We have also studied some organic substances, which theoretically should make good electroreduction accelerators but the predicted catalytic effect was not observed in aqueous solutions. These substances were sparingly soluble in water but well soluble in aqueous-organic solvents. The examples of such species can be the 1,5-diaminonaphtalene (DAN) and N,N′-diphenylthiourea (DFTU) [46] which showed an accelerating effect on Zn(II) reduction in aqueous-alcohol solutions. These compounds undergo adsorption on the electrode surface in the range of Zn(II) ions reduction potentials [46] satisfying the conditions of the cap-pair rule.

The results of our studies indicate that the cap-pair rule holds for the electrode processes occurring in aqueous-organic solvents and the latter constitutes its additional verification and applicability extension.

We have established that, in all studied aqueous-organic solvents, the thiourea decreases activation energy of Zn(II) electroreduction provided the value of activation energy in the selectively hydrated Zn(II) systems is the same. In the solvents with Zn(II) selectively solvated by DMF or DMSO the activation energy decreases and is always lower than the value obtained in aqueous solution [54] as shown in Table 2.

**Table 2.** Values of activation energy of Zn(II) electroreduction in the mixed solvents $H_2O$ + MeOH + 1 M $NaClO_4$ and $H_2O$ + DMSO + 1 M $NaClO_4$ in the absence and presence of TU.

| $c_{MeOH}$ (vol %) | $\Delta H^{\neq}$, kJ mol$^{-1}$ | | $c_{DMSO}$ (vol %) | $\Delta H^{\neq}$, kJ mol$^{-1}$ | |
|---|---|---|---|---|---|
| | $c_{TU}$ = 0.00 M | $c_{TU}$ = 0.25 M | | $c_{TU}$ = 0.00 M | $c_{TU}$ = 0.25 M |
| 0 | 38.3 | 6.1 | 0 | 38.3 | 6.1 |
| 10 | 42.6 | 6.9 | 10 | 22.1 | 6.1 |
| 20 | 58.2 | 6.9 | 20 | 33.7 | 6.1 |
| 50 | 33.9 | 6.1 | 50 | 51.4 | 10.4 |
| 70 | 36.5 | 6.1 | 70 | 53.2 | 34.8 |

The analysis of the experimental results obtained in solvents where Zn(II) is selectively hydrated allowed to formulate the relation between the rate constant of Zn(II) electroreduction in the presence of TU and the degree of electrode coverage with TU [49]. This dependence can be described by the formula:

$$k_{\theta}^{app} = k_{s\theta=1}^{app}\theta + k_{w}^{app}(1-\theta) \qquad (1)$$

where – $\theta$ is the degree of electrode coverage with TU, $k_{s\theta}^{app}$ and $k_{s\theta=1}^{app}$ (the value obtained from extrapolation of log $k_s$ *versus* log $\theta$) are the standard rate constants with a given or complete coverage of the electrode with TU molecules, $k_w^{app}$ is the standard rate constants in the aqueous solution.

We have also found that when the degree of electrode coverage with TU in water and in mixed solvents containing selectively hydrated Zn(II) ions is comparable, the $k_s^{app}$ values for Zn(II) electroreduction do not differ significantly. This indicates that in all cases the reduction of the same form of active complex is taking place (Fig. 4).

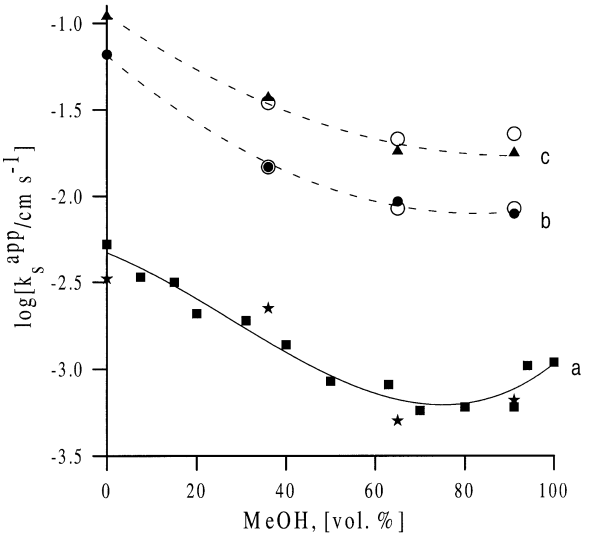

**Figure 4.** Values of the standard rate constants of Zn(II) ions electroreduction in the $H_2O$ + MeOH + 1 M $NaClO_4$mixtures in the presence of: a – 0.00 M TU, b – 0.05 M TU, c – 0.25 M TU *vs.* the mixture composition and the corresponding quantities of rate constants in the aqueous solution with the same degrees of electrode coverage with TU (points – o). On the curve a the points ★ were taken from [57].

However, when electrode coverage with the accelerating substance in water and aqueous-organic solvents containing specifically solvated zinc ions is similar, than the values of standard rate constants obtained in each case are different. The latter suggest different structures of reducing active complex (Fig. 5).

In the process of Zn(II) electroreduction in the solvents containing selectively hydrated and solvated Zn(II) ions, the presence of accelerating substance speeds up the first electron transfer ($k_1$).

This statement holds for apparent values of the rate constants and the so called true rate constants [44,56].

In the presence of the accelerating substance and in the solvents where Zn(II) ion is selectively hydrated the second electron transfer rate constants ($k_2$) take values consistent with the value $k_2$ for the aqueous solutions. However, in all solvents where the selectively solvated Zn(II) ion exists the constants do not change.

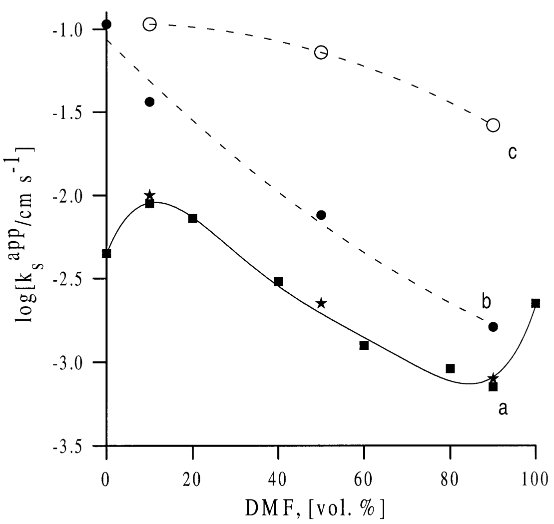

**Figure 5.** Values of the standard rate constants of Zn(II) electroreduction in the $H_2O$ + DMF + 0.9 M $NaClO_4$ mixtures in the presence of: a – 0.00 M TU, b – 0.25 M TU *vs*. the mixture composition and the corresponding quantities of the rate constants in aqueous solution with the same values of the degree of electrode coverage with TU (curve c). The points ★of curve a were taken from [58].

In aqueous-organic solvents the composition of the active complex plays a predominant role in Zn(II) electroreduction acceleration process. The rate of the electrode process depends on the rate of the first electron transfer which increases in the presence of the accelerating substance.

The proposed mechanism of Zn(II) ion electroreduction acceleration on the mercury electrode in the mixed aqueous-organic solvents includes the following stages:

1. The displacement of solvent molecules from the electrode surface by the adsorbing substance.
2. The active complex formation on the electrode surface. The latter is executed by partial replacement of solvent molecules from cation's first solvation layer with the molecules of adsorbed accelerating substance.
3. The transfer of the first electron. The rate of this stage increases in the presence of accelerating substance.
4. The desolvation of ion from the coordination sphere molecules during the second electron transfer.
5. The formation of zinc amalgam.

**Application of the cap-pair effect in the studies of mixed adsorption layers**. Systematic studies of catalysis of metal cation electroreduction allowed to state that the accelerating effects occur in the presence of inhibitors as well. The latter provoked the study of masking and demasking of electrode processes on the dropping mercury electrode, in systems containing two organic substances one of which inhibits and the other accelerates a chosen electrode process. The following systems:

tween 80–thiourea [59], detergents–thiourea and detergents–diaminotoluene [60], ethylene polyglycols–thiourea [61] as well as benzo-15-crown-thiourea [62] were studied with respect to kinetics and adsorption.

It was found that depending on the ratio of inhibitor and accelerating substance concentrations the outcome can either be the inhibition, acceleration or effective compensation of the former two. Beside analytical importance, the results obtained provided information about the occurrence of competitive adsorption and formation of the mixed adsorption layers.

The complex experimental data regarding the adsorption and the kinetics of Zn(II) reduction, when the Zn(II) is considered to conduct the adsorption equilibrium, were obtained. This data was later used to describe the properties and the structure of the mixed adsorption layer at the $Hg/NaClO_{4aq}$ interface. The combination of the above two methods allowed to extend the potential range in which it is possible to trace the adsorption equilibrium in mixed adsorption layers.

If the experimental data for adsorption of surface-active substances on different metals is considered, it appears likely that the mechanism of mixed adsorption layers formation on Hg will be a subject to similar rules. These surface-active reactants can be the popular corrosion inhibitors or substances similar to the latter, in terms of their chemical composition.

In the course of surface-active substance selection, their molecular size and structure were taken into consideration. The inhibitors of Zn(II) ions electroreduction: n-butanol (BU) and ethylene polyglycols with the mean molecular mass 400 (PEG 400) and 10000 (PEG 10000) were used as components of mixed adsorption layers, with thiourea (TU) [63–65] and toluidine isomers: m-toluidine (mT) and p-toluidine (pT) [66–68] were used as the accelerating agents.

To clarify the interpretation of the results acquired in the mixtures of two organic substances, we have chosen a constant inhibitor concentration and a variable concentration of the accelerating substance.

The adsorption equilibrium within the range of the adsorption potential similar to the potential of the zero charge (pzc) was examined according to the classical thermodynamic methodology: the adsorption parameters of the double layer were determined using the Frumkin isotherm and the virial isotherm. The electrostatic parameters of the double layer were determined from the potential drop across the inner layer $\Phi^{M-2}$. The information derived from adsorption measurements is summed up below:

– The values of the relative surface excess $\Gamma'$ of substances accelerating the Zn(II) electroreduction increase together with the increase of the positive charge of the electrode ($\sigma_M$). This is in agreement with the postulated TU molecule orientation on the electrode surface. The sulfur atom of TU is directed towards mercury while toluidine molecules are adsorbed with the aromatic ring. In the presence of all inhibitors studied and in much lower than TU concentrations of toluidine (conditioned by its solubility in the solutions studied), the values of relative surface excess most often decrease in the following order: $\Gamma'_{mT} > \Gamma'_{pT} > \Gamma'_{TU}$.

- In all systems studied the increase in the electrodes' positive charge results in the increase of the value of the free adsorption energy $\Delta G^o$. The latter, according to Payne [69], may be connected with the removal of the water molecules from the surface of the electrode at $\sigma_M > 0$. The linear dependence of $\Delta G^o$ on $\sigma_M$ corresponding mainly to the ion adsorption in the majority of the systems indicates, that the effects connected with the polarity of molecules (stable dipole moment) constitute the dominating impact of the electrode field on the adsorbate molecule.
- The area occupied by a single molecule, calculated from the $\Gamma_s$ value, is larger than the area estimated from the molecular size. This indicates a flat position of the molecules on the electrode surface and their mutual repulsion, which is additionally confirmed by relatively larger values of the virial coefficients. However, this may as well result from the residual presence of other molecules.
- Negligible differences in the adsorption parameters determined for toluidine isomers in the 1 M $NaClO_4$ solution and in the presence of inhibitors indicate that the location of amino groups in the aromatic ring has a limited impact upon the adsorption process. Stronger adsorption of toluidine isomers compared to TU confirms the exceptionally strong impact of the aromatic ring upon the adsorption process [70].
- The values of the interaction parameter A determined on the basis of the Frumkin isotherm indicate repulsive interaction between the adsorbed molecules of the accelerating substance. In all containing TU systems studied, the increase of the electrodes' positive charge was accompanied by the reduction of A parameter resulting from the $ClO_4^-$ penetration between the positively charged amino groups at $\sigma_M > 0$. In solutions containing toluidine isomers the value of the A parameter generally does not depend on the electrode charge which suggests stable orientation of the adsorbed toluidine molecules.
- The linear dependence of the potential drop in the inner layer $\Phi^{M-2}$ on $\Gamma'$ found in the majority of the systems confirms the congruence of the determined adsorption isotherms in relation to the charge. The small values of the inner layer thickness $x_1$ for $\Gamma' = 0$ indicate that the BU and PEG molecules are adsorbed horizontally on the mercury electrode. Relatively large values of electric permittivity $\varepsilon_i$ for $\Gamma' = 0$ ($\varepsilon_i > 10$) obtained in some systems indicate a considerable freedom of inhibitor molecule rotation in the field of the double electric layer.

The results of the Zn(II) ion electroreduction as an ion piloting the adsorption equilibrium in the mixed adsorption layers at a potential distant from the pzc, indicate significantly higher efficiency of toluidine isomers in eliminating the inhibiting impact of PEG as compared to TU. In the systems containing BU the relationship between the concentration of the accelerating agent and the inhibitor, with regard to the compensation effect, is weak. That is it does not depend on the concentration of BU. However, in the presence of PEG, this relationship does occur. The results indicate a higher BU adsorption ability compared to PEG at Zn(II) ion reduction potentials. The latter additionally enables the adsorption of the accelerating agent. It is worth noting that at such potentials, the surface concentrations of the low-molecule substances studied are undoubtedly small and occur in the area of initial, approximately linear, course of the isotherm. This explains the constancy of the relationship between the surface concentration and the bulk concentration. Still, the above relation does not apply to high-molecular compounds.

It should be also noted that Zn(II) ions electroreduction acceleration increases in the presence of all studied inhibitors and is evidenced by the increase of the slope of the straight lines $\log k_s^{app} = f(\log c_{TU,\,pT,\,mT})$ (Fig. 6). The observed effect is associated with the weaker hydration of the adsorption layer.

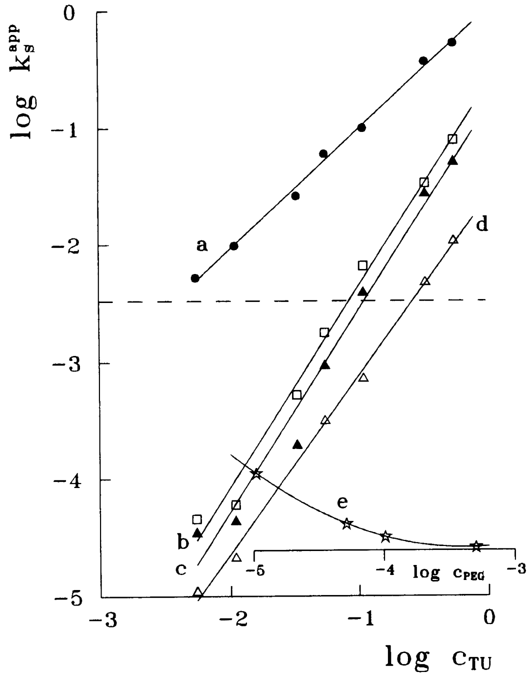

**Figure 6.** Plots of log $k_s^{app}$ for (Hg)Zn ($5 \cdot 10^{-3}$ M)/Zn(II) ($5 \cdot 10^{-3}$ M) couple *vs* log $c_{TU}$ for different contents of PEG. a) $c_{PEG} = 0$ M, b) $10^{-4}$ M PEG 400, c) $5 \cdot 10^{-4}$ M PEG 400, d) $5 \cdot 10^{-4}$ M PEG 10 000 or *vs* log $c_{PEG}$ when $c_{TU} = 0$ M (e). The dashed line denotes $k_s = 3.31 \cdot 10^{-3}$ cm·s$^{-1}$ for the Zn(II) in 1 M $NaClO_4$.

The results of our research provide information which can be used to understand better the adsorption equilibrium generated in complex corrosion systems comprising inhibitors with a specific structure and properties. Effectiveness of toluidine isomers as potential inhibitors of corrosion should be greater than those of TU owing to stronger adsorption of toluidine isomers. This adsorption is conditioned by the metal-aromatic rings' $\pi$ electrons interactions, which come from the partial charge transfer between the adsorbate and the metal. These interactions are the major cause of the horizontal orientation of the adsorbed toluidine molecules. An additional advantage of using toluidine as the inhibitor of corrosion is the fact that, unlike TU, it causes a local increase of pH value.

The discovery of the cap-pair effect and studies of its mechanism disclosed a new role of organic compounds in electrode processes:

- it allowed to state experimentally the formation of mixed adsorption layers and enabled quantitative studies of adsorption processes competitiveness,
- it also extended the range of physicochemical description of adsorption processes,
- and it enabled analytical application of adsorption competitiveness in demasking electrode processes.

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