Polish J. Chem., **78**, 1087–1101 (2004) **REVIEW ARTICLE**

Mixed Adsorption Layers Formed at the Electrode–Solution Interface[*]

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(Received March 1st, 2004; revised manuscript March 29th, 2004)

The current knowledge and most recent advances in the study of mixed adsorption layers on the mercury electrode have been reviewed. Wide spectrum of two-component adsorbate systems containing neutral organic molecules as well as organic and inorganic ions have been presented. The effect of co-adsorption on the kinetics of electrode processes (inhibition in particular) has been discussed.

Key words: adsorption, mixed adsorption layer, mercury electrode, inhibition, acceleration of electrode process

1. Introduction

Co-adsorption of two or more substances results in the formation of mixed adsorption layers. Adsorption of one component influences that of the second one. Due to this interrelation, two types of co-adsorption can be distinguished: adsorption of one component can increase or decrease adsorption of the other one. The latter case is called competitive adsorption. Species of stronger affinity towards the electrode material attenuates adsorption of those of poorer affinity. In principle, one-component adsorption should be also regarded as a competitive process, since ions and dipoles of the supporting electrolyte compete with organic molecules for free adsorption sites. Theoretically, three co-adsorption systems can be distinguished, *i.e.*, ion–ion, ion–organic molecule, and organic molecule–organic molecule.

At the beginning of the 20th century, Gouy [1] discovered co-adsorption of tetraethyl- and tetramethylammonium cations at the mercury–water interface. The author, however, did not provide any surface concentration data for the studied adsorbates.

Surface tension measurements for the mercury electrode in a solution containing two organic substances were originally carried out by Buttler *et al.* [2–4], and were subsequently described by others [5–9]. However, these pioneering endeavours pro-

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

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vided little information about simultaneous adsorption from aqueous solutions containing two different species.

The studies on mixed adsorption layers are of significant practical importance as far as the search for efficient corrosion inhibitors is concerned. Corrosion inhibitors can slow down anodic and/or cathodic processes by either increasing the overvoltage, or blocking the active metal surface. Anodic inhibitors, most frequently anions, cause an increase of the anodic polarization potential, which shifts corrosive potential towards more positive values. Conversely, cathodic inhibitors are usually cations, which block metal surface when deposited on the cathode. For example, As^{3+} and Sb^{3+} inhibit dissolution of iron in aqueous solution containing acids or polyphosphates. In particular, in the presence of Ca^{2+}, the aforementioned species can generate large colloidal cations. Efficiency and versatility of inhibitors may be improved by using their mixtures, *e.g.* cathodic inhibitor combined with an anodic one.

Inhibitors of organic corrosion belong to the same group of compounds as inhibitors of metal etching in acids, or inhibitors of crystal growth. Both are called brighteners, and are used to appropriately regulate deposition of lustrous electroplated coatings. The majority of these compounds contain nitrogen and/or sulfur. Due to their strong adsorption at the entire metal surface, such compounds may simultaneously inhibit cathodic and anodic processes. Corrosion inhibitors act more efficiently when applied together as their binary mixture. Apart from this synergistic effect, antagonistic effect was also noted for certain systems [10]. These phenomena were studied theoretically by applying second order equations. Subsequent examination of the regression coefficients and their significance levels indicated that synergism might occur when the concentration of inhibitors did not exceed 30 mg dm^{-3}. In contrast, when inhibitors were used at the concentration of 100 mg dm^{-3}, antagonistic effect rather than synergistic one was observed.

Synergistic inhibition effect of sodium octylmercaptopropionate and 8-quinolinol was observed during the studies on iron corrosion in aerated 0.5 M Na_2SO_4 [11]. Remarkably high inhibition efficiency of 98.2% was achieved in a mixture containing 3×10^{-4} M sodium octylmercaptopropionate and 5×10^{-4} M 8-quinolinol. It was concluded that strong synergism was due to covering of defects in the iron surface with a precipitate of iron oxide and Fe^{3+} complexes with 8-quinolinol and octylmercaptopropionate.

Corrosion inhibition of mild steel in 1 M H_2SO_4 was studied in the presence of various thiols, *e.g.*, 2-mercaptobenzothiazole, 2-mercaptobenzimidazole, and 2-mercaptobenzoxazole. These organic compounds occurred to be dual-action inhibitors. They affected both anodic and cathodic corrosion processes by blocking the active sites on the metal surface [12]. Since corrosion is charge-transfer controlled process, the presence of electron cloud within the aromatic ring, electronegative atoms (S, N, or O), and easily polarizable heteroatoms was likely to enhance adsorption of thiols on the mild steel surface. This, in turn, led to very effective inhibition. It was also noted that an addition of halides into the corrosive medium containing thiols facilitated inhibition. Similar effect was observed when aspartic acid was added [13].

Comprehensive analysis of the experimental data concerning adsorption of surface-active compounds on different solid metals seems to support a view that mixed adsorption on mercury should proceed analogously. Homogeneity and purity of mercury surface provides excellent reproducibility of adsorption phenomena.

2. Co-adsorption of two neutral organic compounds

Electrocapillary curves have been obtained [14–17] in the presence of 24 different pairs of organic compounds, selected from the following set: tetrabutylammonium sulfate, tetrapropylammonium sulfate, *p*-toluidine, *o*-toluidine, ethanol, butanol, hexanol, propionic acid and capronic acid. The equality of co-adsorption thermodynamic potentials of each two components was assumed. A good agreement between the experimentally determined and calculated surface coverage Θ was observed. Calculations were performed for non-ionic surface-active compounds from the same homologous series [15]. Negative electrode charge facilitated co-adsorption of *n*-butanol–aniline system, whereas positive electrode charge weakened adsorption of aniline in favour of that of *n*-butanol [14]. This effect was attributed to the change in the orientation of aniline molecules following the changes of the electrode charge [16]. In the aminoacetic acid–*n*-butanol system, interactions between *n*-butanol and mercury were weakened compared to those in *n*-butanol–aniline system. This effect was particularly well pronounced at the potentials more positive than PZC (zero charge potential) [17], due to relatively strong interactions between negatively charged carboxylate and positively charged mercury surface. Interactions involving $-NH_3^+$ groups were weaker.

On tensammetric and differential-capacity curves, only one desorption peak for the solution containing two organic compounds was observed. The peak corresponded to the compound, for which the signal was expected to appear at more negative potential [18,19]. Differential capacity curves were utilised for the studies on co-adsorption of numerous two-component systems, *e.g.* bromothymol blue–pyridine, *o*-cresol–amyl alcohol [20], aniline–butanol, aniline–valeric acid, *o*-toluidine–valeric acid [14], thiourea–butanol [21], ethanol–camphor, and ethanol–adamantol [22]. The height and potential of desorption peak for bromothymol blue–pyridine system (fixed concentrations of both components) indicated stronger adsorption of pyridine comparing to that of bromothymol. Also the adsorption mechanism was competitive. In contrast, for *o*-cresol–amyl alcohol system, a surface-active complex was formed. Interestingly, adsorption affinity of the complex was higher than that of each compound separately. In general, as attractive interactions between the molecules of two organic compounds got stronger, desorption peak was being shifted towards more negative potentials [14]. According to differential-capacity curves for *n*-butanol–thiourea system [21], adsorption of thiourea was significantly weaker at the cathode than at the anode. At the maximum adsorption potential one recorded adsorption isotherms at varying concentrations of butanol and at the constant concentration of thiourea. An increase in the concentration of thiourea obviously increased the interaction constant and lowered adsorption energy. It was also reported that an addition of ethanol to the solution of adamantol or camphor [23] lowered the maximum surface excess Γ_s and weakened repulsive interactions between the solute molecules. Russian literature on co-adsorption studies is focused mostly on the determination of theoretical adsorption isotherms under numerous preliminary assumptions. These investigations utilise either two- [22,24–28], or three-parallel capacitor model [29–35]. The former allows one to estimate the coverage Θ as follows:

$$\Theta = (C_0 - C)/(C_0 - C') \tag{1}$$

where C is the capacity of the studied system, C_0 is the capacity at $\Theta = 0$, and C' is the minimum capacity at $\Theta = 1$.

The obtained Θ values were used to calculate adsorption equilibrium constant and interaction constant for *tert*-butanol–trimethylacetic acid system at the selected concentrations of both components [25,26]. Knowing adsorption equilibrium constant for binary mixture and for one of its components, it was possible to calculate it for the other component. Co-adsorption of *tert*-butanol and trimethylacetic acid resulted in a significantly increased adsorption of each component, but only for low and medium coverages Θ. Applicability of this method to the determination of adsorption parameters of other systems, such as hexanol–capronic acid, *n*-butanol–*tert*-butanol, *n*-butanol–*n*-butylamine has been already proved [27]. It was found that for *tert*-butanol–hexanol system [26], Θ_1 for *tert*-butanol was close to Θ_2 for hexanol. Interestingly, Θ value for a binary mixture of these two compounds was always higher than Θ_1 or Θ_2, and often exceeded the sum of Θ_1 and Θ_2.

Three-parallel capacitor model requires various preliminary assumptions to be made, which limits its applicability and often leads to approximate values of adsorption parameters [29,30]. However, this model enables the calculation of theoretical differential capacity curves, electrode charges, and interaction constants to be performed. Indeed, adsorption parameters for both components of binary mixtures were determined after a judicious choice of their concentration: *tert*-butanol–trimethylacetic acid, *tert*-butanol–butyric acid [30], dimethyl adipate–cyclohexanol [31], and *n*-valeric acid–*n*-amyl alcohol [32,33]. Temperature dependence of Θ for *n*-valeric acid–*n*-amyl alcohol systems indicated the interaction constant to be lower than 2. Minimum capacity obtained for this system was slightly lower compared to that of pure components. This was due to beneficial interactions between the functional groups and, in consequence, more ordered and thicker mixed adsorption layer. For *n*-valeric acid–*n*-amyl system, it was also postulated that the orientation of the adsorbed molecules was variable and depended on both the coverage Θ and the electrode charge. Surprisingly, it had no influence on the shape of the corresponding differential-capacity curves, while such effect was observed for the changing orientation of aromatic amides [34]. The changes of the interaction constant for binary systems, the components of which co-adsorb and form single- or multilayered structures [35], have been also studied. For thiourea–butanol and thiourea–butylamine systems [21] it was discovered that repulsive forces between the molecules allowed only one layer to be formed. For thiourea–butylamine system, however, competitive adsorption was more pronounced than for thiourea-butanol system. This was due to stronger specific interactions between the mercury surface and $-NH_2$ groups, than with –OH ones.

Three-parallel capacitor model has also been used to investigate co-adsorption of borneol and butylphenol on a hanging mercury drop electrode [36]. The composition of the mixed adsorption layer was determined. For positive electrode charges, the layer consisted primarily of butylphenol, whereas for lower electrode charges the surface concentration of butylphenol decreased in favour of that of borneol.

3. Co-adsorption of ionic and organic species

Investigations of co-adsorption in ion–organic dipole systems were focused primarily on either the anions of supporting electrolyte, or tetraalkylammonium cations as ionic components. As organic species the compounds of the known adsorption affinity to the mercury surface were used.

More than fifty years ago, Buttler and Wightman reported [37] that adsorption of ethanol and phenol from aqueous solutions decreased in the presence of either bromides or iodides. Subsequent work revealed that introduction of acetanilide to the solution of PO_4^{3-} [38] reduced adsorption of these anions. Nitrates [39] and iodides [40] had similar influence on the adsorption of thiourea. Interestingly, the presence of perchlorates had practically no effect on this process [41]. It was also discovered that thiourea lowered the adsorption energy of iodides, and weakened repulsive interactions between the adsorbed iodide ions [40]. This phenomenon was attributed to the increase of the distance between the mercury surface and the electric centres of the adsorbed iodide ions. In KBr solution the presence of thiourea caused either an increase (at E = const.) or a decrease (at σ_M = const.) of the surface excess of bromides, depending on the choice of electric variable. The latter effect was particularly strong when $\sigma_M > 0$ [42]. One studied also adsorption of thiourea on a mercury microelectrode (drop lifetime: 5.3 ms) [43] from solutions containing either KF or KCl. It was proved that surface excess of thiourea was lower in the presence of chlorides than in the presence of fluorides. Moreover, the amount of the adsorbed chloride ions was lower in the presence of thiourea, compared to the amount adsorbed from pure solutions of NaCl. However, the values of Gibbs energy of adsorption of thiourea were comparable when measured in either NaCl or NaF solution.

Adsorption of chlorides, bromides, and perchlorates resulted in a significant decrease of interaction constant for butanol adsorbed on the mercury electrode [44], and the consequent decrease of peak heights in differential capacity curves. This was consistent with Damaskin theory [45]. Using the theory of co-adsorption of the supporting electrolyte ions and organic molecules [35] it was found that the surface excess of chlorides, bromides, perchlorates, and nitrites increased as the concentration of butanol was increased [46]. However, the surface excess of iodides was not dependent on the concentration of the alcohol. Described effect observed for chlorides, bromides and perchlorates was attributed to attractive interactions between halide ions and butanol molecules, as well as to the weakened interactions between hydroxyl groups and the mercury surface.

It was demonstrated that adsorption of ethanediol in the presence of fluorides, chlorides, bromides, and iodides [47] shifted the PZC towards more positive values. This effect intensified with an increase of the concentration of ethanediol. The shift was the most pronounced in the presence of fluorides and the smallest in the presence of iodides. The results unequivocally demonstrated that positively charged ends of the adsorbed ethanediol dipoles were facing the mercury surface. The presence of ethanediol lowered the surface tension of mercury within the entire range of the applied potentials. This was due to the relatively weak dependence of the Gibbs energy of adsorption $\Delta\overline{G}^{o}$ on the electrode charge. Moreover, adsorbed molecules of ethanediol removed water dipoles, and not anions, from the mercury surface.

It was demonstrated that for co-adsorption of triethyl phosphate and supporting electrolyte anions [48], adsorption of organic component decreased in series: $SO_4^{2-} > ClO_4^- > NO_3^-$. This effect was attributed to the decreased salting effect in these electrolytes and specific adsorption of NO_3^- and ClO_4^- on the mercury surface [49,50]. In turn, attractive forces between studied anions and the molecules of triethyl phosphate increased in the opposite direction, *i.e.*, $NO_3^- > ClO_4^- > SO_4^{2-}$. Surface activity of organic molecules in all the studied systems decreased upon their transfer from the air-solution interface to the solution–mercury interface. Analogous effect was observed for adsorption of alcohols [51], and was attributed to stronger interactions between mercury and water than those between mercury and hydrocarbon chains of alcohols.

It was apparent from the dependence between the hydration energy of halides and their adsorption affinity towards mercury [52] that the former was the main factor governing their specific adsorption. An increase of hydrophilicity of electrode material resulted in a decrease in the surface excess of these ions [53]. It was demonstrated that adsorption of small-radius ions with stable solvation layer was less pronounced than that of large-radius ions, for which desolvation was easier [54]. Adsorption of chlorides and iodides in the presence of poly(ethylene oxide) (average molecular weight 400) was discussed in [55]. Adsorption was not affected by the presence of the polymer, according to the experimentally obtained surface excess values.

Adsorption of tetraalkylammonium cations in the presence of selected organic substances was investigated by analysing differential capacity curves. Tetraalkylammonium cations are symmetrical and their orientation at the electrode surface is independent on their surface coverage. Thus, they are especially appropriate for studying adsorption phenomena. For instance, one investigated adamantol–tetrabutylammonium cation system [56] utilizing hanging mercury drop electrode (HMDE). In the recorded differential capacity curves, two regions were distinguished. For potentials less negative than (–0.6 V) adsorption of adamantol predominated, whereas for $E < -0.6$ V adsorption of cations was the major process. Regardless of the potential range, differential capacity of double layer was slightly increased compared to that observed in the presence of each compound separately. Similarly, the experimentally determined $\Delta\overline{G}^{\mathrm{o}}$ values were lower than those obtained for pure compounds. Interestingly, when tetraalkylammonium cations were used [57], they were not capable of penetrating compact layer formed by adamantol molecules. This was concluded from the calculations of C' values and the potential of maximum adsorption, E_{m}. In comparison to the adamantol–tetraalkylammonium cations, the potential range required for the formation of the layer was narrower. Similarly, each component of β-naphthol–tetraethylammonium cation system was adsorbed preferably within different potential range [58]. These ranges were separated by the peak at the maximum-adsorption potential. The peak reflected the replacement of one component with another in the adsorption layer. This phenomenon could be also explained applying three-parallel capacitor model.

4. Co-adsorption of two different ions

Studies on co-adsorption of two different ions most frequently concern cation–anion systems in solutions of two salts sharing common anion or cation [59]. The influence of the third ion is not taken into consideration. Among cations, tetraalkylammonium and some metal ions are of particular interest. The importance of such studies increases due to the fact that many organic cations are used as inhibitors of metal corrosion [60].

From the comparative studies on co-adsorption of tetrabutylammonium (Bu_4N^+) sulphate and halides, it was concluded that sulphates adsorbed most efficiently in the presence of iodides [61,62]. Co-adsorption of halides in the presence of either metal cations [63] or tetraalkylammonium cations [64,65] increased in series: $Cl^- < Br^- < I^-$. Frumkin isotherm was used to characterize adsorption of Bu_4N^+ from 0.5 M Na_2SO_4 [66], and interaction constant A was calculated. For negative charged electrode $A = 2$, which indicated attractive interactions between the adsorbed ions. The addition of halides to the solution containing Bu_4N^+ led to the significant increase of A. Therefore, competitive effect accompanying co-adsorption in this system was negligible [30]. Presumably, easy deformation of Bu_4N^+ cations was responsible for this phenomenon. Another explanation was that Bu_4NX or $(Bu_4N)_2X^+$ ($X = Br^-$, I^-, SCN^-, ClO_4^-) ion pairs were formed and electrostatic repulsion between Bu_4N^+ and X^- was minimized [67].

Formation of ion pairs can also accompany co-adsorption of choline cations [*i.e.*, $HOCH_2CH_2(CH_3)_3N^+$] and halides [68]. Choline cation comprises hydrophilic (with a hydroxyl group) and hydrophobic (with alkyl groups) fragments. Particular halide ions can be hydrated to various extend [69]. It was observed that hydrophilic OH group had no effect on the adsorption of poorly hydrated ions, such as bromides and iodides. However, their adsorption increased in the presence of long-chain organic compound [70]. The studies on co-adsorption of protonated guanidine and chlorides [71] proved that the presence of specifically adsorbed chloride anions enhanced adsorption of the organic component. Noteworthy, adsorption properties of guanidine cations on mercury differed significantly from those observed for other organic cations. Adsorption of guanidine cations did not lead to the thickening of the adsorption layer, as it was observed for tetraalkylammonium cations. This unusual property indicated horizontal orientation of guanidine cation on the electrode surface.

Competitive effect accompanied co-adsorption of iodides and thiocyanates [72]. Specific adsorption of iodides inhibited that of thiocyanates. Adsorption of iodides from solutions containing either thiocyanates or fluorides proceeded similarly. In contrast, adsorption of thiocyanates from solutions containing iodides differed significantly from that performed from fluorides-containing solutions. Therefore, adsorption of iodides resembled that of neutral organic molecules. Undoubtedly, different geometries of iodide and thiocyanate ions were responsible for this effect. Thiocyanate ions are rather cylindrical and adsorb perpendicularly to the mercury surface through their sulphur atoms [73].

Chronocoulometry and, alternatively, chronopotentiometry are the most frequently utilized methods in the studies on co-adsorption of selected metal cations and anions of supporting electrolyte on the mercury electrode. It was found that adsorption of metal cations is induced by anions, provided that [74]:

a) Anions adsorb specifically on the mercury surface and form complexes with metal cations;

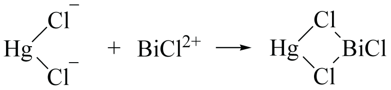
b) Electrode surface is moderately covered with the adsorbed anions. Higher coverage levels make the induced adsorption decrease. This phenomenon is related to steric effects associated with the formation of covalent bonds between tightly packed anions and complex molecules that are about to undergo adsorption.

Mechanism of the anion-induced adsorption of cations was exemplified for Cd^{2+}–$S_2O_3^{2-}$ system [75]:

$$[S_2O_3^{2-}]_{ads} + CdS_2O_3 \rightarrow [Cd(S_2O_3)_2]^{2-}_{ads} \quad (2)$$

Comparing to the Cd^{2+}–I^- system [74,76], surface excess of Cd^{2+} in the solutions containing $S_2O_3^{2-}$ was lower than that in the presence of I^-. Iodides were also found to induce the adsorption of Hg^{2+} and Pb^{2+} [77]. Similarly, adsorption of Cd^{2+} [74], Hg^{2+}, and Pb^{2+} [77] was induced also by bromides. It was reported that SCN^- induced adsorption of Cd^{2+} [78], Hg^{2+} [77,79], Pb^{2+} [77], In^{3+} [80], and Zn^{2+} [81–83]. From the mechanistic point of view, these processes are similar to those occurring in the previously described Cd^{2+}–$S_2O_3^{2-}$ system.

In [84] adsorption of Bi^{3+} (10^{-3} M) induced by chlorides was investigated. It was discovered that the surface excess of Bi^{3+} increased with an increase of the concentration of chlorides, and reached maximum for $[Cl^-] = 0.08$ M. At higher concentrations of chlorides, adsorption of Bi^{3+} decreased. It was established that for $[Cl^-] < 0.03$ M, $BiCl^{2+}$ complex was the predominant species in the solution, and the adsorption proceeded according the following mechanism:



(3)

At $[\mathrm{Cl}^-] > 0.04$ M, BiCl_4^-, in turn, was the predominant species at the electrode surface. For $[\mathrm{Cl}^-]$ ranging between 0.03–0.04 M, both BiCl^{2+} and BiCl_4^- were adsorbed simultaneously. One may conclude that competitive adsorption can be also due to the complex formation.

5. Co-adsorption in mixed solvents

In contrast to other adsorption modes that performed from water–organic solvent mixture was described only in a few literature reports. For instance, adsorption of *o*-toluidine from water–acetone mixture containing 0.1 M LiCl [85] was studied. Introduction of *o*-toluidine resulted in a significant decrease of the surface tension, which was appropriately reflected in electrocapillary curves. However, in the solution containing 20% of acetone, the PZC was constant, irrespective of the concentration of*o*-toluidine. When the acetone content was increased, higher concentrations of *o*-toluidine shifted the PZC towards more negative values. According to the obtained $\Delta\overline{G}^{\circ}$ values, it was concluded that in acetone-free aqueous solutions, orientation of *o*-toluidine molecule depended on the electrode charge. In contrast, in the water–acetone solution, this orientation was fixed within the entire range of applied electrode charges.

Differential capacity curves were used to study adsorption of thiourea from water–methanol [86] and water–ethanol solutions [87]. Relative surface excess of thiourea measured at PZC was shown to be independent on the concentration of methanol, and was slightly lower than that measured in water, however slightly higher than the corresponding values measured in pure methanol. In the case of water–ethanol solutions, the relative surface excess of thiourea decreased with an increasing concentration of ethanol. These effects were a consequence of hydrophobic properties of thiourea [88]. One determined the approximate value of the interaction constant $A = 4$, obtained by shifting the curves of the surface pressure Φ. The value found did not depend on either the concentration of methanol in the solution or the electrode charge. In the subsequent analysis, however, somewhat different results were obtained. By applying the linearity test to the Frumkin isotherm, one found the interaction constant A to range between 3 and 5, and to depend on the electrode charge. In water–ethanol solution, parameter A changed with ethanol concentration. As the mole fraction of ethanol was increased form 0.2 to 0.8, parameter A changed from 2 to 4. To sum up, repulsive interactions between the adsorbed molecules of thiourea shall be attributed to their parallel orientation with respect to the electrode surface. $\Delta\overline{G}^{\circ}$ values for thiourea depended only slightly on the concentration of either methanol or ethanol, and were always lower than those measured for the alcohol-free solution of supporting electrolyte. However, $\Delta\overline{G}^{\circ}$ values obtained in the water–ethanol solution, were always lower than those measured in water–methanol solutions. Moreover, in ethanolic solutions $\Delta\overline{G}^{\text{o}}$ values for thiourea apparently depended on the concentration of ethanol for any electrode charge (except from $\sigma_M = 0$).

For the solutions studied in [86,87], there was a linear correlation between the potential in the inner layer, Φ^{M-2}, and the corresponding values of the relative excess of thiourea. Thus, numerous electrostatic parameters characterising the inner layer could be calculated, in particular electric permittivity, ε_i, thickness, x_i, and integral capacity, K_i. The calculations were carried out using a simple electrostatic model of potential distribution within the inner layer [89]. Such calculations are accurate for electrode charges close to $\sigma_M = 0$ [90]. The obtained electrostatic parameters were higher in the solutions containing methanol than in water–ethanol mixtures. The increased alcohol content resulted in the increased values of the corresponding electrostatic parameters.

6. The effect of co-adsorption on the electrode kinetics

Co-adsorption of organic substances influences the kinetics of electroreduction of metal cations. This effect should be considered in the studies on metal electrodeposition.

Addition of phenols or alcohols into solutions containing β-naphthol had practically no effect on electrodeposition of Cd^{2+} [91]. In contrast, addition of an aromatic amine shifted the half-wave potential by ~0.4 V towards more negative values. Two organic compounds added were capable of inhibiting the electrode process by participating in mutual attractive interactions [91]. This led to the formation of more compact adsorption layer. Slowing down the process of metal electrodeposition is beneficial, since it improves the quality of cathode covering. The latter is more compact and lustrous, due to the presence of smaller microcrystallites in its structure.

Synergistic inhibition was also discovered in isobutanol–Bu_4N^+–Cd^{2+} system [92], and was due to the formation of associates between isobutanol molecules and tetrabutylammonium cations. In consequence high coverage level of organic component was achieved. Good miscibility of the two organic inhibitors (better than their solubility in water) was another property that favoured the occurrence of synergistic inhibition effect [93]. Obviously, significant synergistic inhibition effect was observed when the coverage of the electrode surface with organic compound was not total. Similar effect was observed for isobutanol–Bu_4N^+–Cu^{2+} system, however was less pronounced than for Cd^{2+}.

In *tert*-butanol–trimethylacetic acid–Cd^{2+} system, there was weak chemical interaction between the molecules of both inhibitors. Under such conditions the measured electroreduction rate of Cd^{2+} was not directly related to the rates obtained in the presence of each inhibitor separately [94]. Similar behaviour was observed for dodecylsodium sulfate (SDS)–dodecyl alcohol (DOH)–Cd^{2+} system [95]. SDS is an anionic detergent. In aqueous solution it exists as either a monomer or an associate. Conversely, DOH is the product of SDS hydrolysis. A logarithmic plot correlating the reduction rate constant of Cd^{2+} and SDS concentration was linear, of a slope of (–1). For the mixture of SDS and DOH, the slope reached a value of (–1.56), whereas for aliphatic alcohols its value was (–2) [96]. Such a behaviour was characteristic of a mechanism based on competitive adsorption of the active complex, solvent, and inhibitor [97]. In SDS–DOH mixture, competitive adsorption of both components occurred. Interestingly, for [SDS] > 10^{-4} M, the rate constant of Cd^{2+} reduction increased and at [SDS] ≈ 5×10^{-3} M the rate constant reached the value equal to the one measured in the inhibitor-free supporting electrolyte. Undoubtedly, this effect was related to the formation of SDS micelles in the solution, and polymolecular or micellar layers on the electrode surface. Under such conditions, structural transformation of the micellar SDS adsorption layer by its penetration with DOH was possible. Accessibility of the uncovered electrode surface to Cd^{2+} ions increased their reduction rate (so-called Loskhariev effect, [98–100]). Electroreduction rate constants of In^{3+} measured in the mixtures of cationic and anionic detergents were not directly related to the values measured in the solutions containing each detergent separately [101]. Such detergents are used to diminish maxima in direct-current polarographic reduction waves of In^{3+}. It was found that most of the components of the anionic – cationic detergent couples exhibited antagonistic effect towards the maximum suppression. Interestingly, only trimethylammonium cetyl bromide (cationic detergent) and Tergitol-7 (anionic detergent) both suppressed the maximum.

In alternating current polarography of Cd^{2+}, Pb^{2+}, and Zn^{2+} it was possible to eliminate inhibiting effect of 4-methylcyclohexanocarboxylic acid by adding iodides [102], which form surface-active complexes with metal ions [74,103–106]. In the presence of inhibitor, iodides accelerated electroreduction of Cd^{2+} more than that of Pb^{2+}. This was attributed to the stronger adsorption of iodides in the range of reduction potentials of Cd^{2+}.

Chronopotentiometric studies revealed that in the presence of 10^{-3} M tetrabutylammonium cation, the rate constant of Cd^{2+} reduction increased 100-fold when 1.6×10^{-3} M iodide solution was added [106].

Co-adsorption of two organic compounds, one of which is electroactive, is competitive. For instance, adsorption behaviour of cephazolin and Triton X-100 was studied on a dropping mercury electrode [107]. Surface area occupied by Triton X-100 molecule was estimated as 1.63 mm^2. Reduction kinetics of cephazolin did not depend on the concentration of Triton X-100, however the half-wave potential was shifted to more negative values. It was found that reduction of cephazolin was diffusion-controlled. From the dependence between the cephazolin reduction rate constant and Triton X-100 concentration one concluded the ratio between the number of water molecules displaced by cephazolin and by Triton X-100. This ratio equalled to 0.57.

7. Summary and Conclusions

From the presented results, it is apparent that the formation of mixed adsorption layers on the mercury electrode surface is, most often, accompanied by competitive adsorption. This phenomenon was observed in the following systems: bromothymol blue–pyridine [20], thiourea–butylamine and thiourea–butanol [21], adamantol–ethanol and camphor–ethanol [23], thiourea–X (where X: NO_3^-, I^-, ClO_4^-, or Cl^-) [39–41,43], I^-–SCN^- [72], thiourea–aqueous ethanol (or aqueous methanol) [86,87], active complex–solvent–inhibitor [97], organic substance–organic substance (with one component being electroactive) [107]. The effectiveness of competitive adsorption usually depends on the electrode potential, as it was demonstrated for the following systems: aminoacetic acid–butanol [17], adamantol–tetrabutylammonium cation [56], β-naphthol–tetraacetylammonium cation [58]. For borneol–butylphenol system [36] the effectiveness of competitive adsorption depended also on the electrode charge.

Typical co-adsorption was observed in ethanediol–X (where X: Cl^-, Br^-, or I^-) [47] and poly(ethylene oxide) (M = 400)–X (where X: Cl^- or I^-) systems. In contrast, for butanol–aniline system, co-adsorption occured only for $\sigma_M < 0$. Other electrode charges facilitated competitive adsorption.

In some systems, such as *o*-cresol–amyl alcohol [20], *tert*-butanol–trimethylacetic acid [25,26], *tert*-butanol–hexanol [27], butanol–X (where X: Cl^-, Br^-, ClO_4^-, or NO_3^-) [46], additivity, or even synergism of adsorption was observed. The formation of ion pairs was reported to facilitate adsorption in tetrabutylammonium cation–halides [67], choline cation–halides [68], and guanidine cation–chloride anion systems [71]. Adsorption of selected metal cations induced by the adsorbed supporting electrolyte anions [74–84] was governed by complexation constants in the solution and at the electrode surface.

Wide variety of adsorption mechanisms on mercury is a direct consequence of mutual interactions between adsorbing components, as well as interactions between the adsorbates and the electrode material. Moreover, the electrode charge is also an important factor influencing the nature of the adsorption process.

The effect of co-adsorption on the kinetics of electrode processes was rarely investigated, and efforts in this field were focused primarily on inhibition phenomena. In particular, it was observed that co-adsorption of two inhibitors resulted in synergistic effect, provided that their molecules participated in attractive interaction, or were mutually miscible [93]. Inhibition effect was averaged when interactions between the adsorbed molecules resembled the formation of chemical bonds [94,101]. Adsorption of iodides accompanied by bridging effect decreased the effectiveness of inhibitor [103–106].

Advances in the investigations of mixed adsorption layers formed on mercury electrode may initiate further studies on adsorption on solid electrodes. Within the past few years, competitive adsorption of pyridinethiol and sulfide anions on Au(111) [108], as well as mixed adsorption of octadecanol–1-pyrenenonanol monolayers on Au(111) electrode [109] were studied. Presented above review informations are inspiring source of knowledge for studies of mixed adsorption layers investigated by authors of this paper [110–115].

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