DISSERTATIONES CHIMICAE UNIVERSITATIS TARTUENSIS

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THE KINETICS OF ELECTROREDUCTION OF PEROXODISULFATE ANION ON CADMIUM (0001) SINGLE CRYSTAL ELECTRODE

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1. LIST OF ORIGINAL PUBLICATIONS

1. **T. Thomberg** and E. Lust, Electroreduction of peroxodisulfate anion at Cd(0001) single-crystal plane electrode, J. Electroanal. Chem. 485 (2000) 89–93.
2. **T. Thomberg**, J. Nerut, K. Lust and E. Lust, The kinetics of electroreduction of peroxodisulfate anion on electrochemically polished Cd(0001) plane, Electrochim. Acta 49 (2004) 1271–1279.
3. **T. Thomberg**, J. Nerut, R. Jäger, P. Möller, K. Lust and E. Lust, The kinetics of electroreduction of peroxodisulfate ions on single crystal cadmium and bismuth electrodes, J. Electroanal. Chem (in press, available at www.sciencedirect.com).

2. ABBREVIATIONS AND SYMBOLS

a — center-to-center distance of the ions in a pair

ac — alternating current

C — differential capacitance

$C(f=0)$ — equilibrium capacitance

c_i — bulk concentration of the discharging ion

c_f — base electrolyte concentration

C_dl — double layer capacitance

C_p — parallel capacitance

C_s — series capacitance

cTp — corrected Tafel plot

D — diffusion coefficient

E — electrode potential

e_0 — elementary charge

edl — electrical double layer

EP — electrochemically polished

F — Faraday constant

f — alternating current frequency

f_0 — activity coefficient

GCSG — Gouy-Chapman-Stern-Grahame model

j — current density

j_d — limiting current density

j_k — kinetic current density

K_A — association constant

k_cor — rate constant corrected for the double layer effect

k_het — apparent rate constant of the heterogeneous reaction

N_A — Avogardo constant

n_i — number of electrons consumed in the reaction of the ion

R_p — parallel resistance

SHE — standard hydrogen electrode

T — absolute temperature

x — distance of the reaction site from the outer Helmholtz plane

x_i — location of the effective point charge at a certain distance

Z'' — imaginary component of the impedance

Z' — real component of the impedance

z_eff — effective charge number of a reactant ion

z_i — charge number of a reactant ion

4M CE — calomel electrode in 4 M KCl

α — transfer coefficient

α_app — apparent transfer coefficient

ε — dielectric constant of the solvent

κ — Gouy screening length (i.e. the inverse Debye lengt)

ν — rotation velocity

σ — surface charge density

ψ_0 — potential drop in the diffuse layer (outer Helmholtz plane potential)

ψ_1 — electrical potential at the optimum point, where the charge transfer from metal to ion take place

ω — angular frequency

3. INTRODUCTION

Electroreduction of the peroxodisulfate anion has been suggested as a probe reaction for studying the influence of the electrical double layer (edl) structure on the charge transfer mechanism from a metal to an anion [1–29]. Experimental data for Hg [1–4,13–17] and various polycrystalline sp-metals like Bi, Sb, Pb, Sn, Cd and Ag [5–9], as well as for single-crystal Ag(111) and Ag(100) planes [8,9] in the limited concentration region of the base electrolyte solution have implied that the reduction rate of the overall two-electron peroxodisulfate anion is controlled by a single one electron rate-determining step. It should be noted that the $S_2O_8^{2-}$ electroreduction reaction is irreversible due to breaking of the O–O bond [3–7,30–32].

There is no systematic experimental data and analysis of electroreduction of $S_2O_8^{2-}$ anion on the so-called “mercury like” solid electrodes with the regular surface structure (i.e. for single crystal Cd, Bi etc electrodes) in various base electrolyte systems. The main aim of this study is to analyse and compare the experimental data obtained for $S_2O_8^{2-}$ electroreduction on the Cd(0001) single crystal plane electrode in NaF and Na_2SO_4 base electrolyte solutions, as well as to test the applicability limits of the various theoretical and empirical approximations and to characterise the charge transfer mechanism.

4. KINETIC PARAMETERS OF ELECTROREDUCTION

The reduction rate of the overall two-electron peroxodisulfate anion is controlled by a single one electron rate-determining step. This rate-determining step can be characterised by an apparent rate constant k_{het} of the heterogeneous reaction [4–6]

$$k_{\text{het}} = k_{\text{cor}} \exp(-z_i F\psi_1/RT) = k_0 \exp(-z_i F\psi_1/RT)\exp[-\alpha F(E-\psi_1)/RT] \quad (1)$$

where k_{cor} is the rate constant corrected for the double layer effect (so-called Frumkin correction (ψ_1 effect)); ψ_1 is the electrical potential at the optimum point, where the charge transfer from metal to ion takes place; z_{i} is the charge number of a reactant ion, α is the transfer coefficient; and k_0 is the potential-independent rate constant. As shown and discussed in Refs. [15–33], the classical conception is oversimplified even for the Hg electrode [18–21]. It should be noted, that the very low values of the apparent transfer coefficient α_{app} ($\alpha_{\text{app}} = 0.22$ if $z_{\text{i}} = -2$) have been reported [1–5,30–33] and, according to Gierst [10], α_{app} depends on the electrode potential ($\alpha_{\text{app}} \approx 0$ at $E \leq E_{\sigma=0}$, if $z_{\text{i}} = -2$; and $\alpha_{\text{app}} \approx 0.2$ or 0.4 at $E << E_{\sigma=0}$, if $z_{\text{i}} = -1$). Thus, as it was pointed out in Ref. [10], there is a noticeable change in a mechanism from an activationless discharge of the divalent anion to a normal discharge of the univalent ion-pair [31,32]. Results of quantum chemical calculations [28,33] show that the electroreduction of the $S_2O_8^{2-}$ anion belongs to the group of the reactions with a very complicated mechanism and the transfer of the first electron to the $S_2O_8^{2-}$ anion takes place according to Eq. (2)

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{-*} . \quad (2)$$

it was found that the transfer of the first electron is probably the rate determining step and the standard potential for the redox couple

$E^0_{S_2O_8^{2-}/SO_4^{2-};SO_4^{-*}}$ =1.45 V versus SHE [25–28,33]. According to the experimental results, there is no specific adsorption of the $S_2O_8^{2-}$ anions on the Hg electrode and the reaction centre lies in the diffuse layer [1–9,17,27,28]. The very low values of α_{app} for the Hg electrode have been explained theoretically by Petrii et al. [19,28,33] by the diabatic and activationless charge transfer mechanism [31,32].

It should be noted that Damaskin et al. [30] have discussed the possibility to use the new diffuse layer theory developed by Gonzalez and Sanz [34] where the activity of the $S_2O_8^{2-}$ anions at the outer Helmholtz plane has been used as the concentration variable to construct the so-called corrected Tafel plots (cTp) [35]. It was found that for Hg | $K_2S_2O_8$ + K_2SO_4 system the new model gives reasonable results (with $\alpha_{app} = 0.11$), but for Hg | $K_2S_2O_8$ + KF system the influence of the activity of the anions and corresponding corrections are very small [30].

According to the new so-called microscopic double layer ψ_i potential correction model [24,28,29,33,36–42], the interaction of reactants with the electrical double layer field can be modelled on the basis of the so-called "microscopic ψ_i" approach, taking into account the effective charges of the atoms forming the complex ions.

Another more usual representation is based on the location of the effective point charge at a certain distance x_i with subsequent calculation of the effective value z_{eff} [2–4,36–42]. In the papers published by Frumkin and Petrii et al. [2–7,43,44], there has been developed a formal conception taking into account that the ψ_1 potential is different from the Gouy-Chapman diffuse layer potential ψ_0 for aqueous NaF base electrolyte solution and the effective double layer potential at the reaction site, $\psi_x(x_i)$, has been calculated as [24,35]

$$\psi_{\mathrm{x}}(x_{\mathrm{i}}) = \frac{4RT}{F}\operatorname{arctanh}\left\{\tanh\left(\frac{F\psi_0}{4\mathrm{RT}}\right)\exp(-\kappa x)\right\} \tag{3}$$

where ψ_0 is the classical Gouy – Chapman diffuse layer potential for the base electrolyte, and κ is the Gouy screening length (i.e. the inverse Debye length) for the electrolyte solution with concentration c, and κ is expressed as

$$\kappa = \left(\sqrt{\frac{\varepsilon_0 \varepsilon RT}{2cF^2}}\right)^{-1} \tag{4}$$

In Eq. (3), the variable $x = x_{\mathrm{i}} - x_0$ is a distance of the reaction site from the outer Helmholtz plane with distance x_0 from the electrode surface and the potential drops linearly from the value of ϕ^{m} at the interface to the value ψ_0 at the outer Helmholtz plane ($\psi_{\mathrm{x}}(x_{\mathrm{i}}) = \phi^{\mathrm{m}} - (\phi^{\mathrm{m}} - \psi_0)\frac{x_{\mathrm{i}}}{\mathrm{x}_0}$) if the reaction site lies in the inner layer region [24].

For electroreduction of the $\mathrm{S_2O_8^{2-}}$ anion on Hg it was found that the linear corrected Tafel plots can be established if the reaction site is assumed to lie in the inner layer, i.e. at the distance somewhat smaller than the parameter of the effective ellipsoid formed by the $\mathrm{S_2O_8^{2-}}$ anion (0.32 nm and 0.68 nm respectively) [4,24,28,29,33,45]. However, for electroreduction of $[\mathrm{Fe(CN)_6}]^{3-}$ ions on Hg very large values of the distance from the outer Helmholtz plane, x, have been established (i.e. $x \geq 1.0$ nm) [5,7,43–45] and according to these data this distance is more than two times larger than the effective diameter of the $[\mathrm{Fe(CN)_6}]^{3-}$ ion (equal to 0.41 nm) [39]. Thus, the double layer correction for electroreduction of the complex anions at the so-called Hg-like metals in various base electrolyte solutions is an open question.

5. EXPERIMENTAL

Solutions were prepared from the triply recrystallised from the Milli-Q+ water NaF, Na_2SO_4 and $Na_2S_2O_8$ salts. The Milli-Q+ water was used for preparation of the solutions studied. Air was removed from the solutions by bubbling argon (Ar, 99.998%) through or over solution prior to or during measurements, respectively.

Electrochemically polished (EP) Cd(0001) single crystal plane electrode used was prepared according to the methods described in Refs. [34,46–48]. After the electrochemical polishing the Cd(0001) electrode was rinsed carefully with Milli-Q+ water and submerged into the solution at $E = -1.2$ V vs. calomel electrode in 4 M KCl (4MCE). Electrochemical measurements were performed at $T = 298$ K in a three-compartment glass cell with a separated platinum counter electrode, as well as by a separated (by Luggin capillary) reference electrode (calomel electrode in 4 M KCl).

Conventional electrochemical equipment (Pine Company) was used for the stationary and rotating disc voltammetry (rotation velocity $\nu = 0\ldots9990$ rev min^{-1}). Dependence of differential capacitance C on the electrode potential E was measured using Autolab PGSTAT with FRA2 system [49]. The differential capacitance was evaluated for the equivalent circuit consisting of a resistor and a capacitor in series and measured at ac frequencies f from 0.1 to 1000 Hz. The equilibrium capacitance values $C(f = 0)$, obtained by the linear extrapolation (in the region $0.5 \leq f \leq 500$ Hz), have been used for calculating the charge density vs. electrode potential dependences. It should be noted that in this region of ac frequencies, the $C_s,(2\pi f)^{1/2}$ plots are linear and there is a nearly ideal capacitive behaviour of the Cd(0001) electrode in the base electrolyte solutions, i.e. the Z'', Z'-plots can be fitted by the parallel combination of the "true" double layer capacitance C_{dl}, parallel capacitance C_p and parallel resistance R_p, demonstrating very high R_p values at $E \geq -1.5$ V (Z'' and, Z' are the imaginary and real components of the impedance, respectively). The classical diffuse layer potential ψ_0 has been calculated using the Gouy-Chapman-Grahame model [1–6], and for Na_2SO_4 additionally the Gonzalez-Sanz theory [34] has been used.

For the accurate determination of precision of the experimental data, a statistical treatment of the results was carried out. A total number of independent experiments $n \geq 8$, and at least two different electrodes with the same crystallographic orientation were used [34,46–49]. The relative error in current density at E = const. did not exceed 4…9%.

6. RESULTS AND DISCUSSION

6.1. Cyclic and rotating disc electrode voltammetry data for electroreduction of the peroxodisulfate anion at Cd(0001)

The experimental voltammograms of the peroxodisulfate anion reduction at the EP Cd(0001) electrode in $Na_2SO_4 + Na_2S_2O_8$ aqueous solutions are displaced in Fig. 1a (corrected for the current densities for the base electrolyte solution). According to the experimental results, the current densities for Cd(0001) in the base electrolyte solution are noticeably smaller than those for the system with addition of $S_2O_8^{2-}$ anion and only at very negative potentials ($E \leq -1.5$ V versus 4 M CE) there is a weak increase of cathodic current weakly dependent on the rotation velocity of the disk electrode (Fig. 2). Thus, the kinetically limited process established is probably hydrogen evolution at $E < -1.5$ V as the current density at fixed potential only slightly increases with the base electrolyte concentration. On the other hand, the very week specific adsorption of cations at the EP Cd(0001) plane is possible [46–49] (Fig. 3a). The dependence of the differential capacitance on the cation hydration energy in the region of the diffuse layer minimum potential, taken equal to the zero charge potential $E_{\sigma=0}$ for 1:1 electrolyte, (C increases in the order LiF < NaF < KF) indicates the complicated cation coadsorption process which is caused by the weak specific adsorption of F^- anions near the zero charge potential and by the changes in the diffuse layer structure [4,21–23,50–54]. For that reason, all from kinetic data were calculated from the experimental j, E curves within the range $-1.7 \leq E \leq -1.1$ V for Cd(0001), taking into account the current densities in the base electrolyte solution.

According to the data in Fig. 1, the electroreduction rate of $S_2O_8^{2-}$ to SO_4^{2-} depends noticeably on the electrode potential and on the base electrolyte concentration. Differently from Au electrodes [18–21] no hysteresis of current density between the negative and positive scans of potential was observed for

Cd(0001) plane in the region of mixed kinetics if $c_{\mathrm{Na_2S_2O_8}} \leq 1\times10^{-4}$ M. In the case of higher $c_{\mathrm{Na_2S_2O_8}}$, the hysteresis of the *j*, *E*-curves has been established and it increases with increasing $c_{\mathrm{Na_2S_2O_8}}$. As there is no hysteresis in the *j*, *E* curves for the pure base electrolyte solutions (NaF, Na_2SO_4), it seems that the slow adsorption of $S_2O_8^{2-}$ (or the intermediate product of the reaction), discussed by Frumkin in [4, p. 234], is possible. Therefore the data for solutions with $c_{\mathrm{Na_2S_2O_8}}$ more than 1×10^{-4} M for Cd(0001) have not been used for the quantitative analysis of the edl effects and calculation of the corrected Tafel plots. In the region of zero charge potential ($-1.1 \leq E \leq -1.0$V vs. 4M CE for Cd(0001)), the very well exposed current plateaus were found, better established for Na_2SO_4 compared with NaF solutions (Fig. 2). The current density values (*j*) at $E = \text{const.}$ measured at the rotating EP Cd(0001) disc electrode (at $v > 1500$ rev min^{-1} and corrected for the current densities for the base electrolyte solution) were found to fit well to the Levich ($j,\omega^{1/2}$) plot [31,32] ($0.997 \leq R^2 \leq 0.999$)

$$j_d = 0.620 n_i F \upsilon^{-1/6} D^{2/3} \omega^{1/2} c_i \tag{5}$$

where j_d is the limiting current density, n_i is the number of electrons consumed in the reaction of the ion *i*; c_i is the bulk concentration of the discharging ion; υ is the kinematic viscosity; ω the angular frequency ($\omega = 2\pi v$) and *D* is the diffusion coefficient. Taking $n_i = 2$ and $\upsilon = 0.01$ cm^{2}s^{-1} [1–9], the diffusion coefficient of the peroxodisulfate anion has been calculated for a 5×10^{-3} M Na_2SO_4 in solution ($D = 1.15\times10^{-5}$ cm^{2}s^{-1}) which is in a good agreement with NaF +$Na_2S_2O_8$ system [21,22] and with literature data [4–8]. Thus, in this region of potentials, the electroreduction of the $S_2O_8^{2-}$ anion on the EP Cd(0001) plane is mainly limited by the diffusion step of the $S_2O_8^{2-}$ anions to the electrode surface.

According to Fig. 1, with increasingly negative polarization ($E < -1.1$ V versus 4 M CE for Cd(0001)), the inhibition of $S_2O_8^{2-}$ electroreduction begins, caused by the rise of the negative value of the ψ_1 potential as well as by repulsion of the negatively charged $S_2O_8^{2-}$ anions from the electrode surface. In the dilute base electrolyte solutions a cathodic minimum of current density at $-1.5 \leq E_{\text{cat}} \leq -1.3$ V (4M CE) was found for the Cd(0001) electrode. In comparison with NaF + $Na_2S_2O_8$ system, this minimum is shifted toward more negative potentials in the case of Na_2SO_4 + $Na_2S_2O_8$ system, which is caused by more negative zero charge potential in the base electrolyte solution. Difference in the differential capacitance minimum potentials in the C, E curves for NaF and Na_2SO_4 solutions, ΔE_{min}, varies from –0.03 to –0.04 V, depending slightly on c_{NaF} and $c_{Na_2SO_4}$. The results in Fig. 3b show that at $E < -1.4$ V the differential capacitance values increase with rising $c_{Na_2S_2O_8}$ in the solution, but at $-1.4 < E -0.95$ V (4M CE) the values of C decrease with increasing $c_{Na_2S_2O_8}$. It should be noted that the C_s, E- as well as Z'', Z'-plots, can be fitted by the equivalent circuit where the adsorption of one reacting particle has been taken into account [55,56]. However, the results of fitting for the dilute $Na_2S_2O_8$ solutions show that the influence of adsorption is comparatively weak and the adsorption of the $S_2O_8^{2-}$ anions can be neglected to a first approximation. There is only a weak shift of the minimum potential in the C, E-curves with $c_{Na_2S_2O_8}$ (Fig. 3c). Thus, for Cd(0001) plane the $S_2O_8^{2-}$ adsorption and surface blocking is possible only in the case $c_{Na_2S_2O_8}$ higher than 3×10^{-4} M.

At more negative surface charge densities ($E \leq -1.5$ V (4M CE)), acceleration of $S_2O_8^{2-}$ anion electroreduction occurs as $d\psi_1/dE \approx$ const. in this potential region. Acceleration of reaction is mainly caused by the increase of the negative electrode potential, as well as, probably, by the beginning of the weak specific adsorption of the base electrolyte cations at the negatively charged surface of the EP Cd(0001) electrode. This result is in a good agreement with the impedance data (Fig. 3a) as in this region of potentials ($E < -1.5$ V (4M CE)) the weak rise of the differential capacitance values with c_{NaF} and $c_{\mathrm{Na_2SO_4}}$ was observed [46–48]. For Cd(0001) plane in this region of potentials, the current density mainly linearly increases with increase of the base electrolyte concentration (Fig. 1). Thus, at the very negatively charged Cd(0001) surface the exchange of the electroreduction mechanism of $S_2O_8^{2-}$ anions is possible, i.e. additionally to the usual charge transfer process the simultaneous charge transfer through the adsorbed ion-pairs is probable. It should be noted that for more concentrated base electrolyte solutions ($c_{\mathrm{Na_2SO_4}} \geq 3\times10^{-2}$ M), the corrected current densities are lower than the limiting diffusion currents at $E > -1.1$ V (vs. 4 M CE). This effect can be explained by adsorption of the Na^+ ions and co-adsorption of the $S_2O_8^{2-}$ ions [1–7,21–23,41,42] and by formation of the $Na^+S_2O_8^{2-}$ ion pairs in the inner layer region of the electrical double layer (i.e by the so-called “surface blocking effect”, caused by adsorption of the reaction intermediates or reactants). This effect seems to be important only for the more concentrated base electrolyte systems because the adsorption of Na^+ cations on Cd(0001) is very week.

6.2. Kinetic analysis

The kinetic current densities j_k have been obtained from the linear ($0.996 \leq R^2 \leq 0.999$) Koutecky-Levich plots at constant potential according to the Frumkin, Aikazyan, Tedoradze and Koutecky method [2–8,31,32,57,58]. The values of j_k are somewhat higher for Na_2SO_4 (compared with NaF) solutions, which is in a good agreement with the higher ionic strength values for the electrolyte system studied and with the Frumkin slow discharge theory

[2–7]. The apparent rate constant of the heterogeneous reaction of the electroreduction of $S_2O_8^{2-}$ anions, k_{het}, was defined by Eq. (6)

$$j_k = n_i F k_{het} c_i \qquad (6)$$

where c_i is the bulk concentration of the discharging ion.

Figs. 4a and 4b demonstrate the statistically treated log k_{het},E dependences for EP Cd(0001) plane (obtained from the current densities corrected for the base electrolyte current densities). As it can be seen, the values of log k_{het} decrease with dilution of the base electrolyte but the decrease of k_{het} is somewhat smaller than that predicted according to the Frumkin slow charge transfer theory [4–6]. Statistical analysis of the log k_{het}, E plots shows that the values of log k_{het} for Cd(0001) do not depend on the reactant concentration if it is less than 2×10^{-4} M (Fig. 4c). At higher $c_{S_2O_8^{2-}}$ the small decrease of log k_{het} begins at fixed E, indicating the possible weak adsorption of the reactant or reaction intermediates on the Cd(0001) plane (i.e. the so-called surface blocking effect [16–18] has been established caused by the adsorption of the $S_2O_8^{2-}$ anions or reaction intermediates at the Cd(0001) electrodes). At higher $c_{S_2O_8^{2-}}$ the small rise in k_{het} has been observed, indicating the change of the reaction mechanism. For EP Cd(0001) electrode the weak dependence of k_{het} on the geometrical structure of the base electrolyte anion (i.e. ionic strength) has been established only in the region of moderate base electrolyte concentrations (from 1×10^{-3} to 1×10^{-2}M). The values of k_{het} for the EP Cd(0001) plane are somewhat lower than those for Au(hkl) [19,20].

6.3. Corrected Tafel plots

The corrected Tafel plots (cTps) [35] have been calculated using various empirical approximations for the ψ_1 potential value [1–9,28–42]. At first the classical Frumkin approximation was used (i.e. it was assumed that $\psi_1 = \psi_0$ and

$z_i = -2$ for the $S_2O_8^{2-}$ anion). As it can be seen in Figs. 5a and 5b, the corrected kinetic current density values decrease noticeably with increasing c_f at fixed $(E - \psi_0)$.

The cTps (corrected for $c_{S_2O_8^{2-}}$) for EP Cd(0001) plane in solutions with constant c_f coincide at higher negative polarisations if $c_{Na_2S_2O_8} \leq 2\times10^{-4}$M (Fig. 5c). However, the values of slope of the cTps (and thus the transfer coefficient α_{app} obtained from the slope) are regularly lower for Na_2SO_4 compared with NaF base electrolyte solutions (Fig. 6). The slope of the cTps for the Cd(0001) electrode decreases with increasing c_{NaF} ($\alpha_{app} = 0.14$ for 0.002 M NaF and $\alpha_{app} = 0.11$ for 0.03 M NaF) (Fig. 5a, 6), but the opposite tendency is valid in the case of Na_2SO_4 (Fig. 5b, 6). The slope values of cTps are practically independent of $c_{S_2O_8^{2-}}$ in solution if $c_{S_2O_8^{2-}} < 2\times10^{-4}$ (Fig. 5c) but there is a weak dependence of α_{app} on $c_{S_2O_8^{2-}}$ if $c_{Na_2S_2O_8} \geq 2\times10^{-4}$M.

The charge transfer mechanism through the adsorbed ion-pairs has been discussed by Frumkin and coworkers [2–7]. The data for Cd(0001) | NaF + $Na_2S_2O_8$ system show (Fig. 7a) that noticeably less pronounced dependence of the corrected kinetic current values on c_f has been established if the ion-pair formation at the outer Helmholtz plane (i.e. in the reaction zone) has been taken into account [5–7]. Thus, if we assume that $z_i = -1$ and $\psi_1 = \psi_0$ then there is a better concordance of the cTps in the region $0.005 \text{ M} \leq c_{NaF} < 0.03$ M and in the region of moderate surface charge densities $\sigma \approx -10{,}0$ to $-4{,}0$ μC cm^{-2}. However, there is not so good accordance of cTps for Cd(0001) | Na_2SO_4 + $Na_2S_2O_8$ (Fig. 7b) system in the wider region of the base electrolyte concentrations compared with NaF system. The cTps are nonlinear near the zero charge potential and deviation of cTp toward the higher values of corrected current densities can be established in contradiction with Gouy-Chapman and Frumkin slow discharge theories [2–7,59–62]. At $E << E_{\sigma=0}$, the weak dependence of the slope of cTps on c_f has been established, indicating the dependence of α_{app} on c_f (Fig. 8).

A good coincidence of cTps can be established if we assume that the charge number, i.e. the effective charge of the $S_2O_8^{2-}$ anions depends on the electrode potential as well as on the base electrolyte concentration (Fig. 9a). The effective charge number has been calculated using the Frumkin-Petrii method [2–7]. The results of calculation show that the comparatively low absolute values of z_{eff} have been obtained, depending weakly on the chemical nature of the base electrolyte studied (Fig. 9b). The decrease in $|z_{eff}|$ at $E << E_{\sigma=0}$ in the case of Cd(0001) indicates the adsorption of cations on the electrode surface and the exchange of the reaction mechanism, i.e. the cationic catalysis is possible at $\sigma << 0$ [1–7,33].

As mentioned in Ref. [39] the ionic association process of the polycharged complex anions (including SO_4^{2-} and $S_2O_8^{2-}$ anions) with the base electrolyte cations is possible in the solution phase. The ionic association process in the solution phase has been simulated according to the Fuoss equation [63]

$$K_A = 4\pi N_A a^3 e_0^{\ b} / 3000 \qquad (7)$$

where $b = e_0^{\ 2} / a\varepsilon kT$, e_0 is the elementary charge, ε is the dielectric constant of the solvent and N_A is the Avogadro number. The values of the association constant K_A, calculated according to Eq. (7) assuming that the distance of the closest approach of various ions a = 0.36; 0.6 and 0.8 nm, are comparatively low (K_A = 0.118 for 0.36 nm). In these conditions, the kinetic current density is expressed as [41]

$$j_k = kc_1 \exp\left[\frac{-\alpha(E-\psi_0)F}{RT}\right]\exp\left[\frac{-z_i F\psi_0}{RT}\right] + k_A c_2 \exp\left[\frac{(-z_i+1)(F\psi_0)}{RT}\right] \qquad (8)$$

where $z_i = -2$ (charge of the $S_2O_8^{2-}$ anion) and ($z_i + 1$) is the charge number of associated $S_2O_8^{2-}$ anion with Na^+ (base electrolyte cation); k_A is the relative rate constant for the reduction reaction of the reactant with $(z_i + 1) = -1$ ($NaS_2O_8^-$); c_1 and c_2 are the effective volume concentrations of the $S_2O_8^{2-}$ anion and $NaS_2O_8^-$ ion complex, respectively; and k is the rate constant [39]. The results calculated by Eq. (8) for Cd(0001) plane demonstrate a very large difference between the cTps in the case of 0.002 and 0.03 M NaF as well as Na_2SO_4 base electrolyte solutions and, therefore, the ionic association in the solution phase has not a remarkable influence on the shape and coincidence of cTps for the Cd(0001) | $Na_2S_2O_8$ + NaF or Na_2SO_4 systems.

According to the results of classical works [2,4,5,7,43,44], the linear corrected Tafel plots for Hg | $S_2O_8^{2-}$ system were obtained if it was assumed that the reaction site lies in the inner layer (i.e. $x_i - x_0 < 0$), but for Hg | $[Fe(CN)_6]^{3-}$ system the reaction site has to lie in the diffuse layer ($x = x_i - x_0 > 0$). The results of simulation of the data for the EP Cd(0001) in $Na_2S_2O_8$ + NaF or Na_2SO_4 aqueous solutions show that in spite of the selected fixed values of $x = x_i - x_0 > 0$ (0; 0.23; 0.43; 0.68 nm) in Eq. (3) the cTps obtained are nonlinear and there is no concordance for cTps measured in a wide concentration region of the base electrolyte (Fig. 10). The values of the apparent transfer coefficient are comparatively low and depend on concentration of the base electrolyte in the solution (Fig. 8).

Analysis of the experimental Tafel plots shows that the coincidence and linearity of the cTps (Fig. 11) at $E < E_{\sigma=0}$ can be obtained if we assume that the distance of the closest approach of the reacting anions to the electrode surface, $x = x_i - x_0$, depends on the base electrolyte concentration (i.e. $x = f(c_f)$). Analysis of the cTps for Cd(0001) plane shows that the concordance of cTps can be reached if the term in the last brackets of Eq. (3) $[-\kappa(x_i - x_o)] \approx$ const. at

$E = \text{const}$. Thus, if we assume that the diffuse layer theory is correct [59–62] (and the Gouy length κ can be calculated using this theory) and the value of the ψ_x potential at the reaction site can be calculated using Eq. (3) then it is possible to calculate the effective distance values of the reaction site from the outer Helmholtz plane $x = f(c_f)$, assuming that the cTps have to be linear and coincide for different c_f. The results in Figs. 11 and 12 show that this is valid if we assume that x is an exponential function of the base electrolyte concentration. Thus, if this effect has a real physical background then we can conclude that the effective distance of the reaction site from the EP Cd(0001) surface (as well as from the outer Helmholtz plane) increases exponentially with diluting the electrolyte solution, i.e. with increasing the effective ion atmosphere according to the Debye – Hückel theory. According to Fig. 12, a better fit of the experimental data has been established in the case of comparatively small x values for more concentrated base electrolyte solutions and, thus, the reaction site lies not far from the outer Helmholtz plane for the EP Cd(0001) plane.

The weak dependence of the effective distance of the reaction site on the chemical nature of the base electrolyte anion can be explained by the different so-called “squeezing out” effects [4–7,46–49,59–62], i.e. by the dependence of the distance of the closest approach [50,64–67] of the reacting ions to the electrode surface on the base electrolyte concentration and geometrical structure of the anion.

It should be noted that there are deviations from the classical Gouy-Chapman-Grahame model for Cd(0001) electrode in NaF and Na_2SO_4 solutions with different concentration [46–54] i.e. the inner layer capacitance depends on the electrolyte concentration. The electrical double layer (i.e. ψ_0-potential) correction for the systems with the weak specific adsorption of anions is a very complicated problem even for systems with the constant ionic strength where no electrochemical reaction occurs [50–54]. The systematic analysis of experimental data for Bi(hkl) [53,57] as well as Cd(0001) electrodes [46–48,61] shows that the ψ_0-potential values calculated using classical Gouy-Chapman-Grahame model [59–62] are overestimated (i.e. the negative values of ψ_0 are too large to give the linear corrected virial isotherms at $\sigma < 0$). The situation is more complicated for the systems with the smaller ionic strength. Thus, it can be concluded that the classical $|\psi_0|$ potential corrections are too high to give the concordance for the cTp-s at $\sigma << 0$ within the wide base electrolyte conentration region. This conclusion is in a good agreement with the results for $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$ electroreduction on Bi(hkl) and Cd(0001) electrodes [41,42].

Comparison of the ψ_0 values with the ψ_x potential values (calculated according to Eq. (3) assuming that $x = f(c[Na_2SO_4])$), shows (Fig. 13) that the values of $|\psi_x|$ are somewhat lower than $|\psi_0|$ and at very high negative surface charge density ($E < -1.4$ V versus 4 M CE) there is only a weak dependence of ψ_x on c_f if $c_f \geq 2\times10^{-3}$ M. Thus, at comparatively negative surface charge densities the influence of diffuse layer (i.e. the base electrolyte concentration) on the charge transfer kinetics is very small caused probably by the charge transfer through the adsorbed ion-pairs [2,5,7,30–32].

The data in Fig. 14 show that the values of transfer coefficient α_{app}, obtained from Fig. 11, are practically independent of the base electrolyte concentration. However, α_{app} for NaF is higher than that for Na_2SO_4 base electrolyte (Fig. 14). The very low values of α_{app} for the EP Cd(0001) | base electrolyte + $Na_2S_2O_8$ systems indicate that the activationless electroreduction process is possible at high negative surface charge densities (i.e. at $E << E_{\sigma=0}$), which is in a good agreement with the Levich model [31,32] and data for the Hg electrode [28,33].

Fawcett et al. developed a model for the diffuse layer potential correction based on the generalised field spherical approximation [68–70], but the corrections obtained using Fawcett model only weakly differ from those obtained according to the Gouy-Chapman-Stern-Grahame (GCSG) model as the comparatively dilute base electrolyte solutions ($c_{\mathrm{NaF}} \leq 5\times10^{-2}$ M and $c_{\mathrm{Na_2SO_4}} \leq 0.03$ M) have been used in our studies.

According to the Gonzalez-Sanz model for the diffuse layer [34] and Damaskin et al. analysis [30] the activity of the electrolyte in spite of concentration should be used as the so-called concentration variable [30]. These corrections are small for the NaF solutions but in the case of Na_2SO_4 solutions the linear C_{ex}^{-1},C_{ca}^{-1} plots (i.e. the experimental capacitance vs. calculated diffuse layer capacitance according to the Gonzalez-Sanz theory plots) have been established (Fig. 15) only by using Gonzalez-Sanz model. The values of the inner layer capacitance C_{H} in the case of Na_2SO_4 are in a good agreement with those for NaF. The dependences of the kinetic current density, corrected for the medium activity coefficient according to the model by Gonzalez-Sanz [34], on the electrical variable E are given in Fig. 16. For Cd(0001) | $Na_2S_2O_8$ + base electrolyte systems (Fig. 16) the less pronounced dependence of corrected current density on c_{f} has been established in comparison with the cTps obtained using classical Frumkin correction [2–7,14].

7. FIGURES

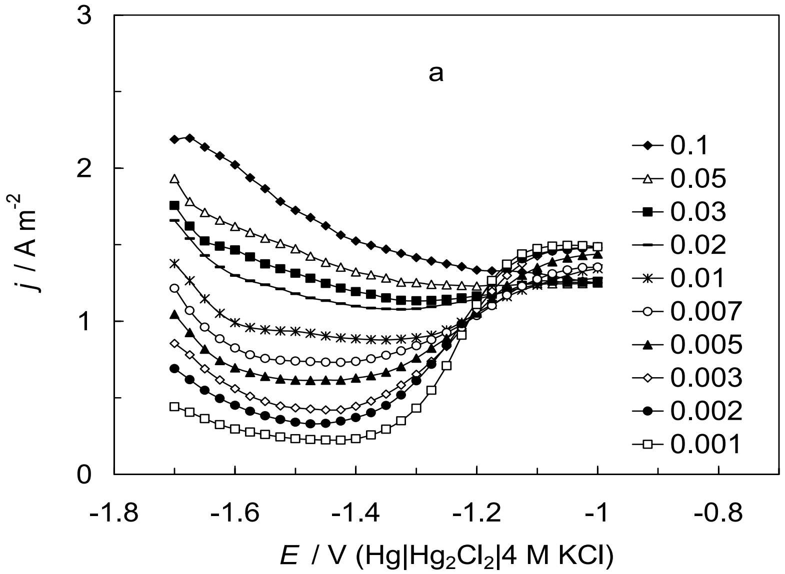

Fig. 1a

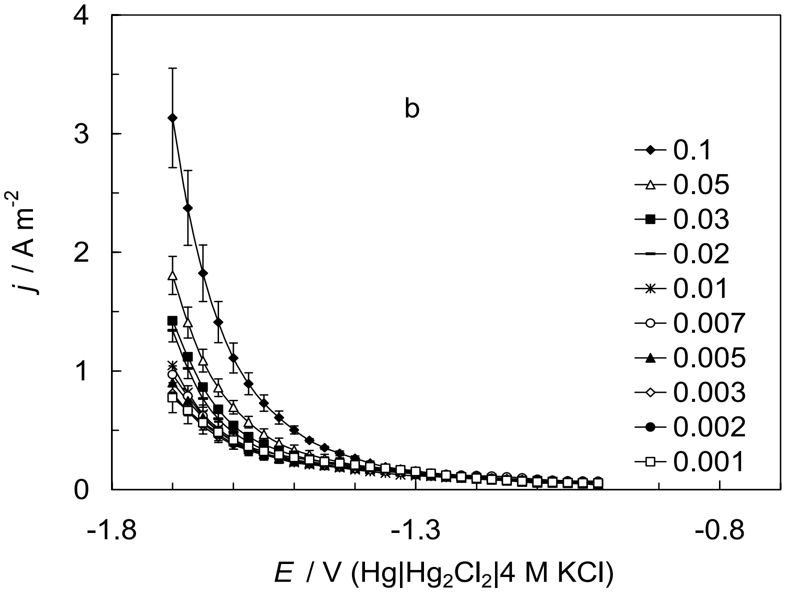

Fig. 1b

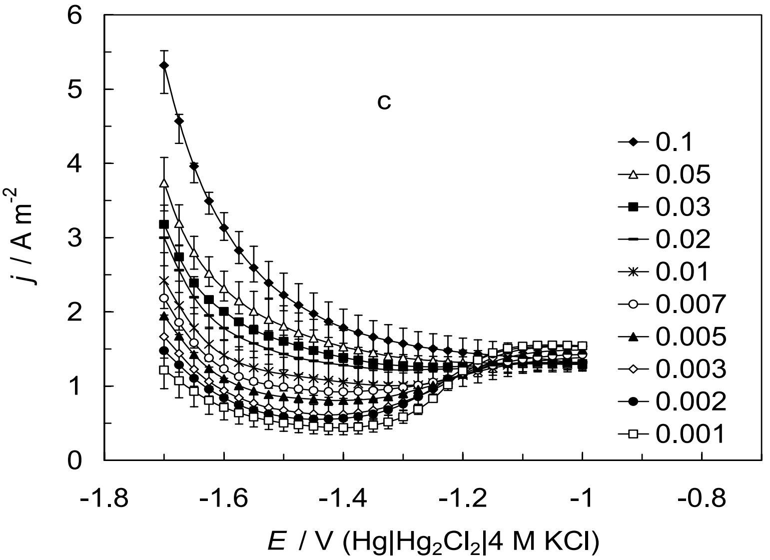

Fig. 1c

Fig. 1. Rotating disc voltammetry curves (scan rate 10 mV s^{-1}; rotation velocity $\nu = 9000$ rev min^{-1}) for the electrochemically polished (EP) Cd(0001) plane in 4×10^{-5} M $Na_2S_2O_8$ + x M Na_2SO_4 solution (x, noted in figure) corrected for base electrolyte current densities (a); uncorrected curves in the different base electrolyte solutions (b); and curves for 4×10^{-5} M $Na_2S_2O_8$ in the base electrolyte solution with different concentrations (M), noted in figure (c).

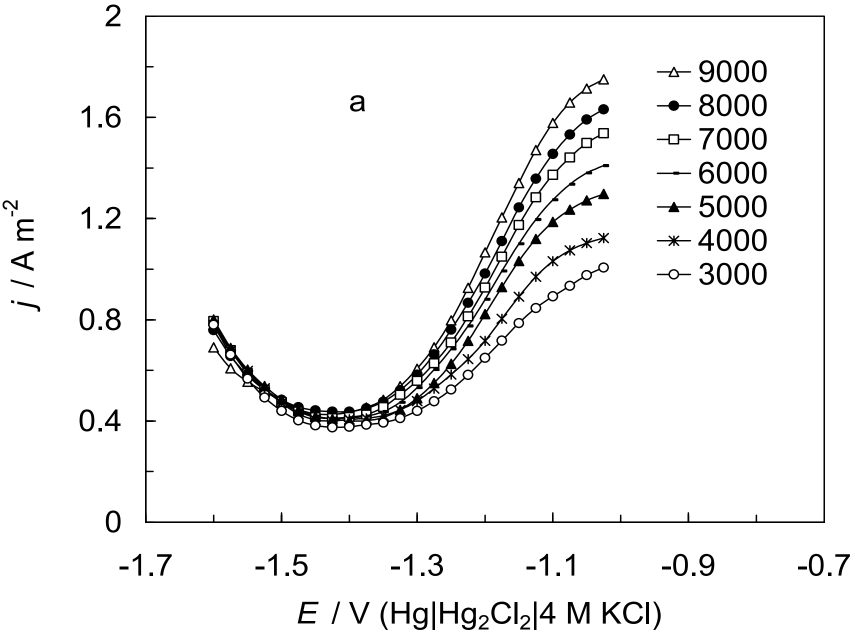

Fig. 2a

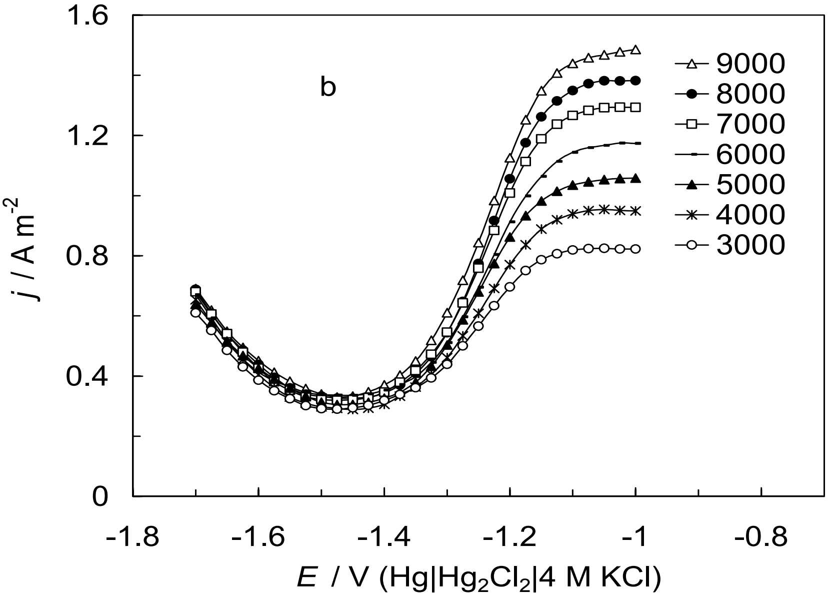

Fig. 2b

Fig. 2. Rotating disc voltammetry curves (scan rate 10 mV s^{-1}) for the EP Cd(0001) plane in 4×10^{-5} M $Na_2S_2O_8$ + 2×10^{-3} M NaF solution (a) and for 4×10^{-5} M $Na_2S_2O_8$ + 2×10^{-3} M Na_2SO_4 solution (b) (corrected for the base electrolyte current densities) at rotation velocities (rev min^{-1}), noted in figures.

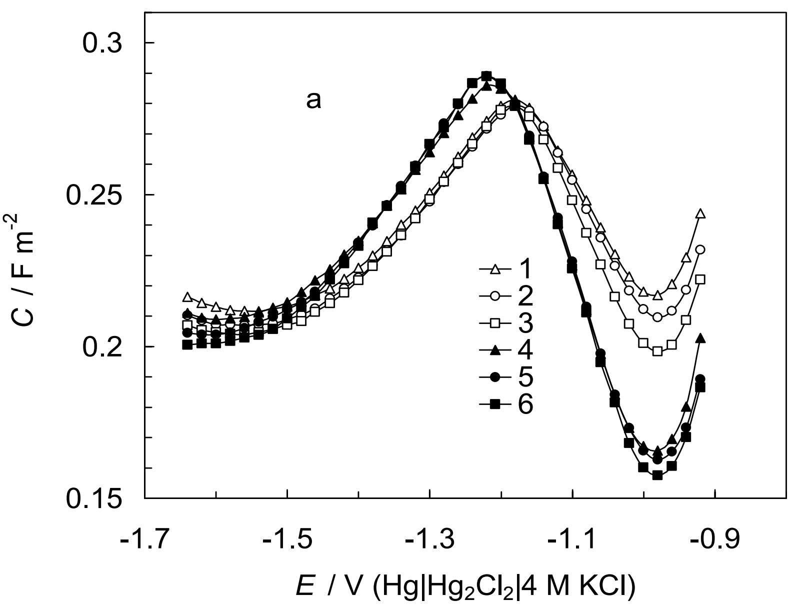
a
0.3
0.25
0.2
0.15
-1.7
-1.5
-1.3
-1.1
-0.9
C / F m^{-2}
E / V (Hg|Hg$_2$Cl$_2$|4 M KCl)
1
2
3
4
5
6

Fig. 3a

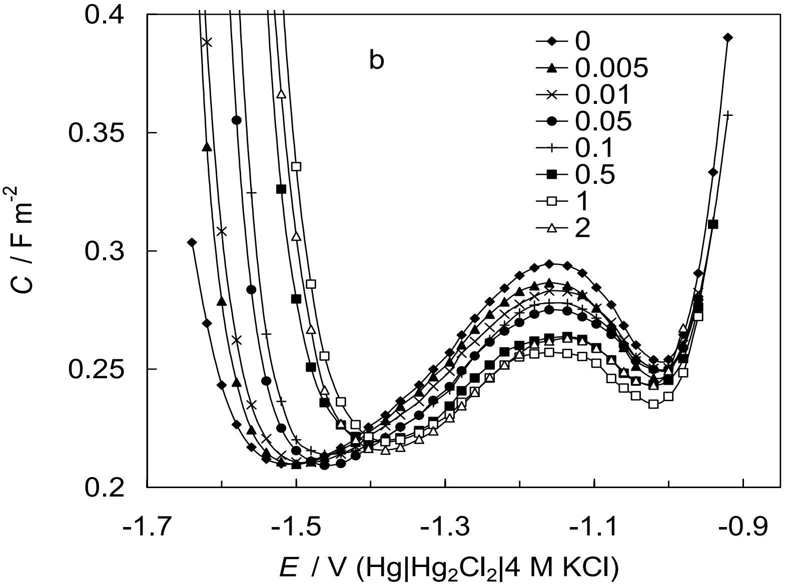
b
0.4
0.35
0.3
0.25
0.2
-1.7
-1.5
-1.3
-1.1
-0.9
C / F m^{-2}
E / V (Hg|Hg$_2$Cl$_2$|4 M KCl)
0
0.005
0.01
0.05
0.1
0.5
1
2

Fig. 3b

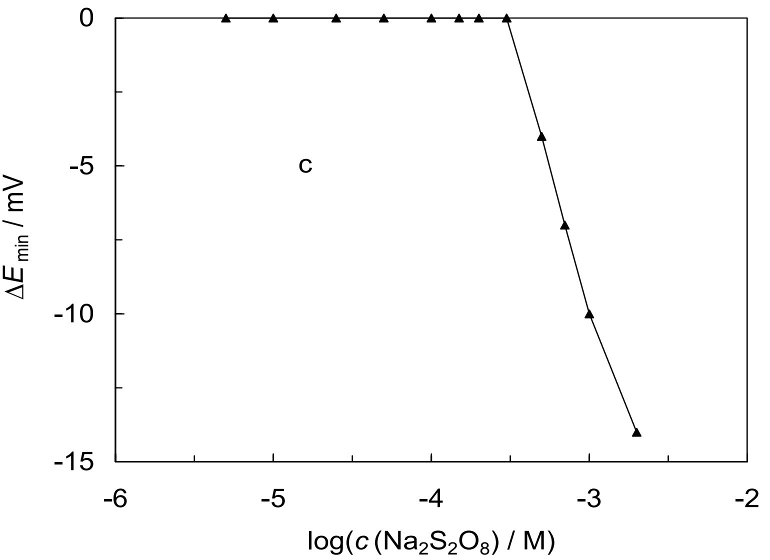

Fig. 3c

Fig. 3. Differential capacitance vs. electrode potential curves (ac frequency *f* = 20 Hz) for Cd(0001) plane in 0.01 M (1; 2; 3) and 0.003 M (4; 5; 6) KF (1;4), NaF (2;5) and LiF (3;6) solutions (a); in 1×10^{-2} M Na_2SO_4 + *x* mM $Na_2S_2O_8$ with *x* (mM), noted in figure (b); ΔE_{min},$\log c_{Na_2S_2O_8}$ dependence for Cd(0001) electrode (c).

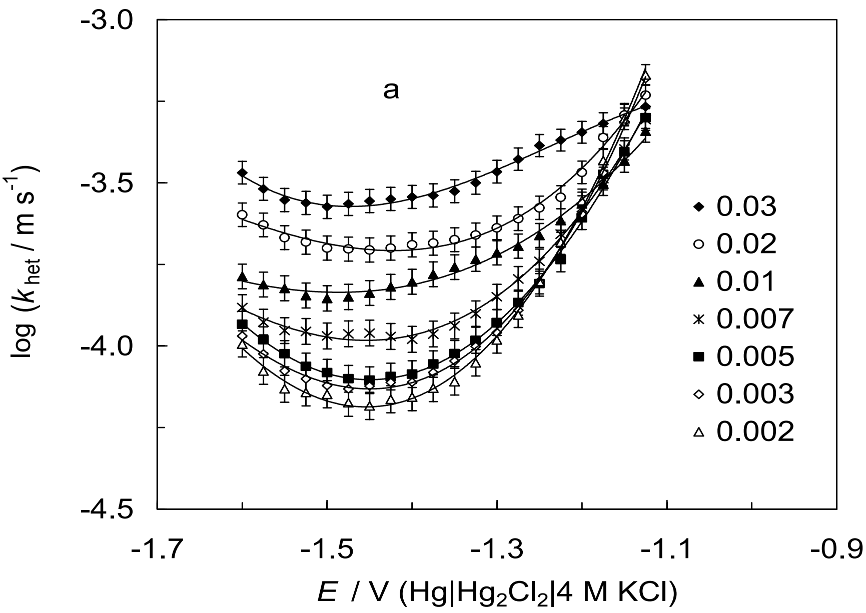
a
-3.0
-3.5
-4.0
-4.5
log (k_{het} / m s^{-1})
-1.7
-1.5
-1.3
-1.1
-0.9
E / V (Hg|Hg$_2$Cl$_2$|4 M KCl)
◆ 0.03
○ 0.02
▲ 0.01
✳ 0.007
■ 0.005
◇ 0.003
△ 0.002

Fig. 4a

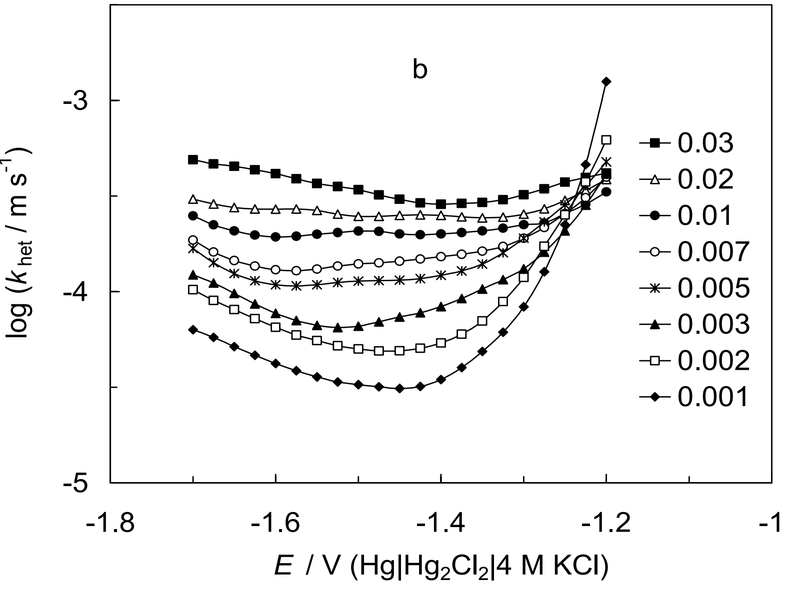
b
-3
-4
-5
log (k_{het} / m s^{-1})
-1.8
-1.6
-1.4
-1.2
-1
E / V (Hg|Hg$_2$Cl$_2$|4 M KCl)
■ 0.03
△ 0.02
● 0.01
○ 0.007
✳ 0.005
▲ 0.003
□ 0.002
◆ 0.001

Fig. 4b

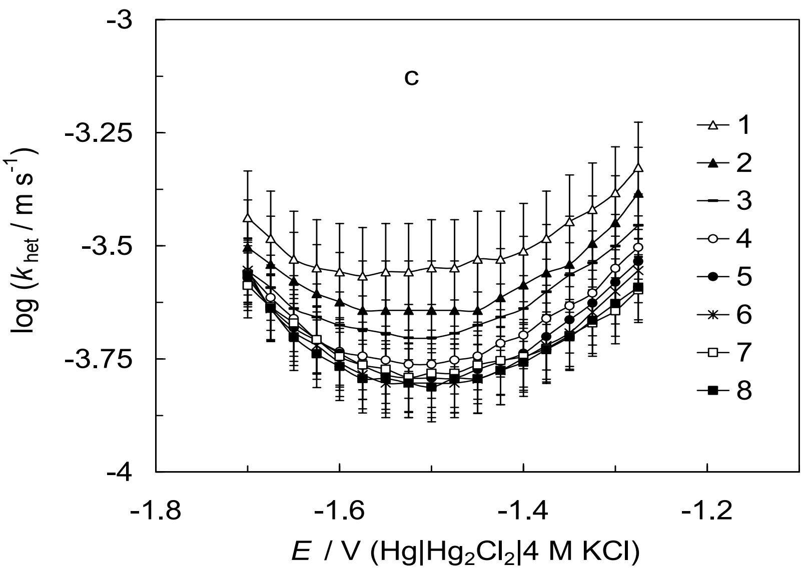

Fig. 4c

Fig. 4. Heterogeneous rate constant vs. electrode potential dependences (obtained from the j, E curves corrected for the base electrolyte current densities) for EP Cd(0001) electrode: (a) in 4×10^{-5} M $Na_2S_2O_8$ solution with different additions of the base electrolyte NaF (M), noted in figure; (b) in 4×10^{-5} M $Na_2S_2O_8$ solution with different additions of the base electrolyte Na_2SO_4 (M), noted in figure and (c) in 1×10^{-2} M Na_2SO_4 with different additions of $Na_2S_2O_8$ (M): 1 — 1×10^{-3}; 2 — 7×10^{-4}; 3 — 4×10^{-4}; 4 — 2×10^{-4}; 5 — 1×10^{-4}; 6 — 7×10^{-5}; 7 — 4×10^{-5}; and 8 — 2×10^{-5}.

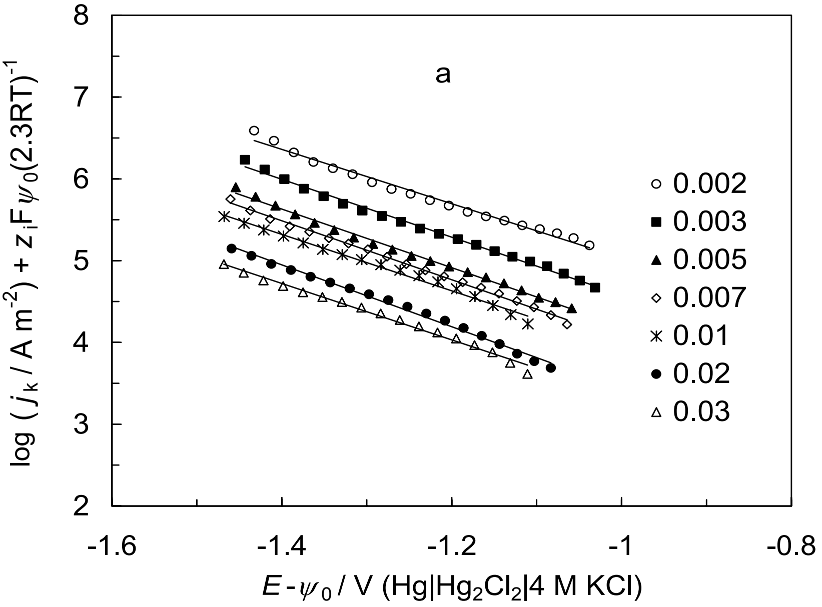
a
$\log(j_k / \mathrm{A\,m^{-2}}) + z_i F \psi_0 (2.3RT)^{-1}$
8
7
6
5
4
3
2
-1.6
-1.4
-1.2
-1
-0.8
$E - \psi_0$ / V (Hg|Hg$_2$Cl$_2$|4 M KCl)
○ 0.002
■ 0.003
▲ 0.005
◇ 0.007
✳ 0.01
● 0.02
△ 0.03

Fig. 5a

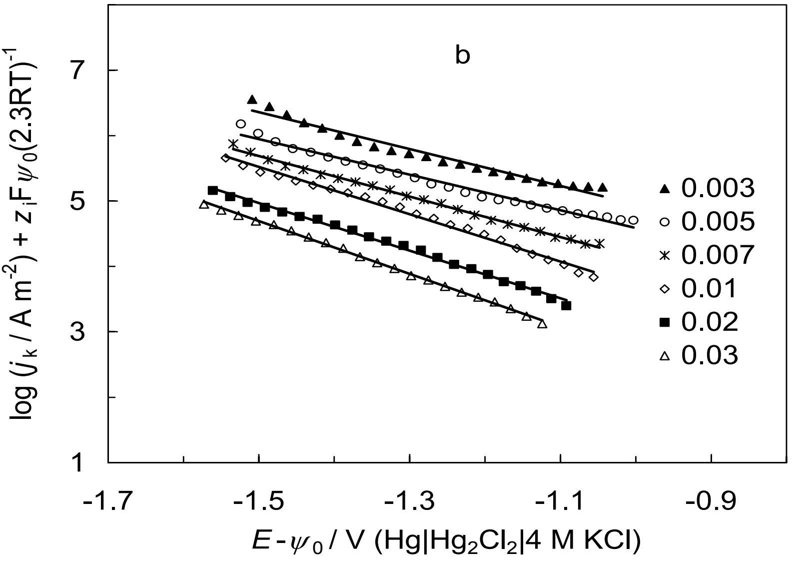
b
$\log(j_k / \mathrm{A\,m^{-2}}) + z_i F \psi_0 (2.3RT)^{-1}$
7
5
3
1
-1.7
-1.5
-1.3
-1.1
-0.9
$E - \psi_0$ / V (Hg|Hg$_2$Cl$_2$|4 M KCl)
▲ 0.003
○ 0.005
✳ 0.007
◇ 0.01
■ 0.02
△ 0.03

Fig. 5b

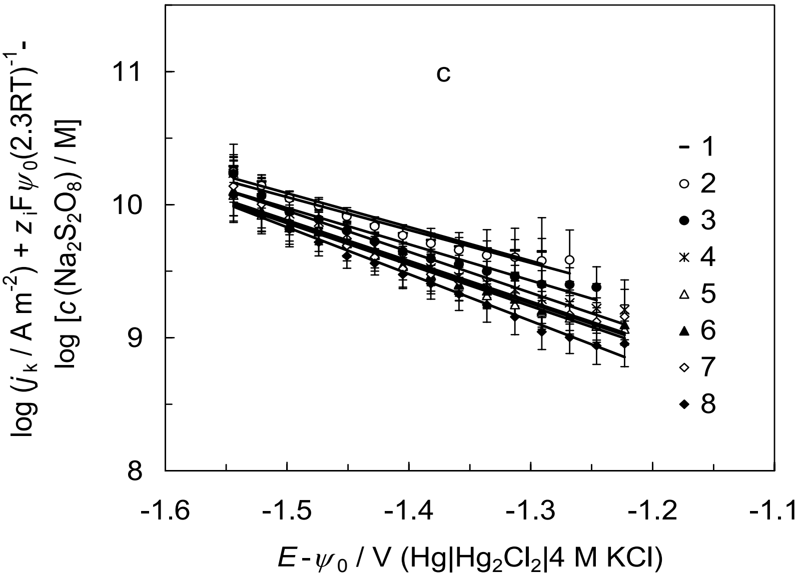

Fig. 5c

Fig. 5. Corrected Tafel plots (cTp) ($z_i = -2$ and $\psi_1 = \psi_0$, i.e. classical Frumkin correction) for the EP Cd(0001) plane: in 4×10^{-5} M $Na_2S_2O_8$ solutions with different additions of NaF (M), noted in figure (a); in 4×10^{-5} M $Na_2S_2O_8$ solutions with different additions of Na_2SO_4 (M), noted in figure (b); and in 1×10^{-2} M Na_2SO_4 solutions with different additions of $Na_2S_2O_8$ (M) (c): 1 — 1×10^{-3}; 2 — 7×10^{-4}; 3 — 4×10^{-4}; 4 — 2×10^{-4}; 5 — 1×10^{-4}; 6 — 7×10^{-5}; 7 — 4×10^{-5}; and 8 — 2×10^{-5}.

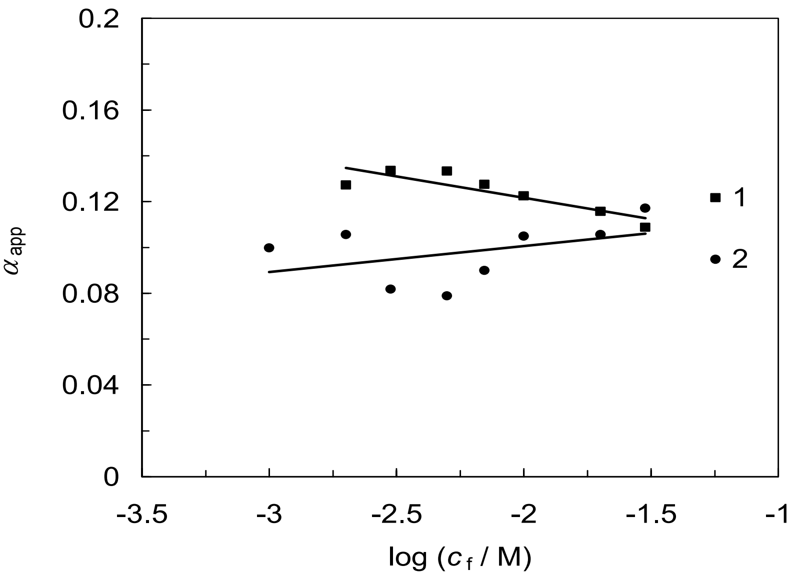

Fig. 6. Apparent transfer coefficient vs. log c_f dependences for Cd(0001) in the NaF (1) and Na_2SO_4 (2) solutions.

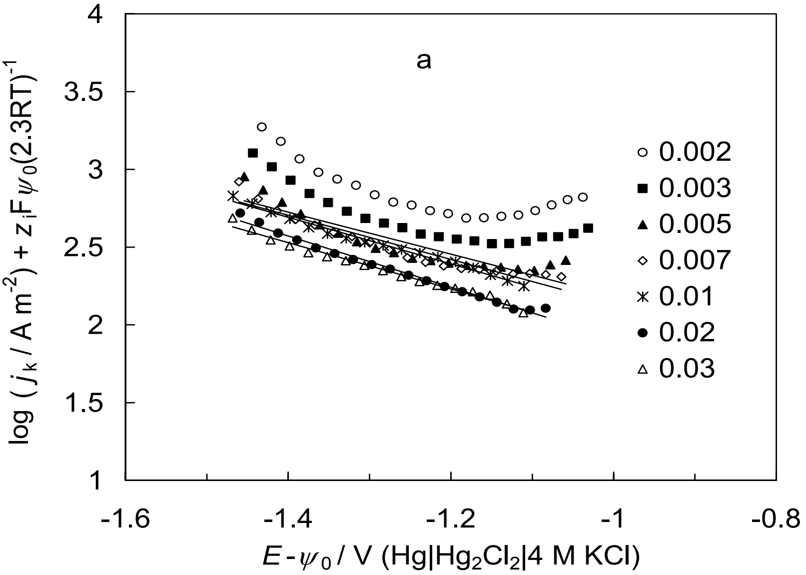

Fig. 7a

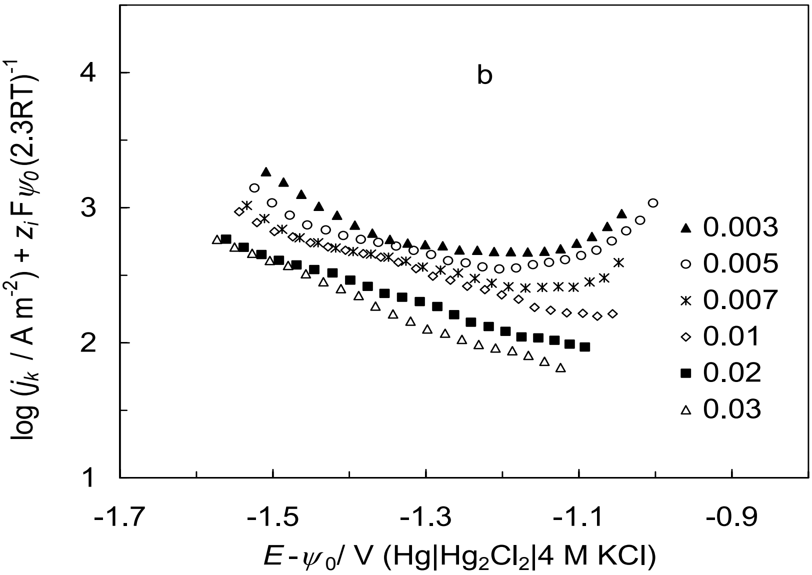

Fig. 7b

Fig. 7. Corrected Tafel plots at the conditions $\psi_1 = \psi_0$, $z_i = -1$ for the EP Cd(0001) plane: in 4×10^{-5} M $Na_2S_2O_8$ solutions with different additions of NaF (M), noted in figure (a); in 4×10^{-5} M $Na_2S_2O_8$ solutions with different additions of Na_2SO_4 (M), noted in figure (b).

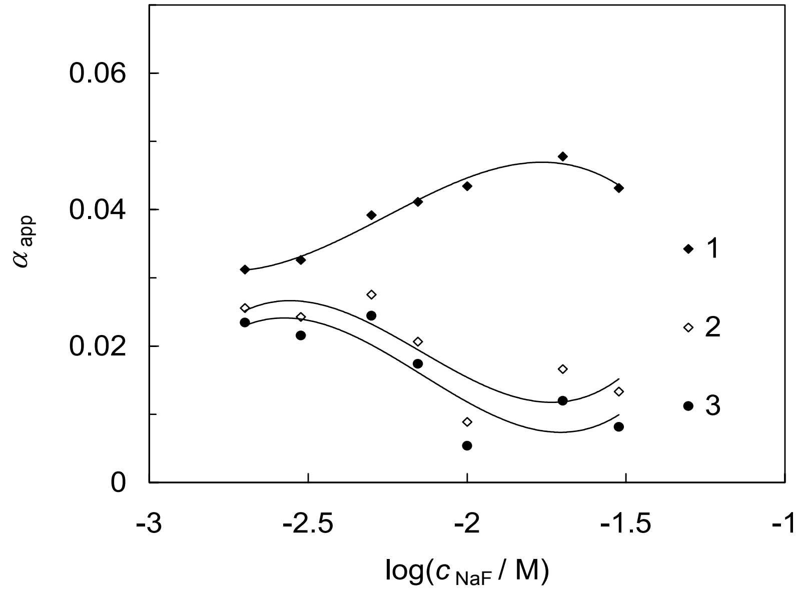

Fig. 8. Apparent transfer coefficient vs. logc_{NaF} dependences calculated at various approximations of the ψ_1 potential: $z_i = -1$, $\psi_1 = \psi_0$ (1); $z_i = -2$ and ψ_x calculated according to Eq. (3) at the fixed distances of reaction site from the outer Helmholtz plane, x (nm): (2) 0.20 and (3) 0.43.

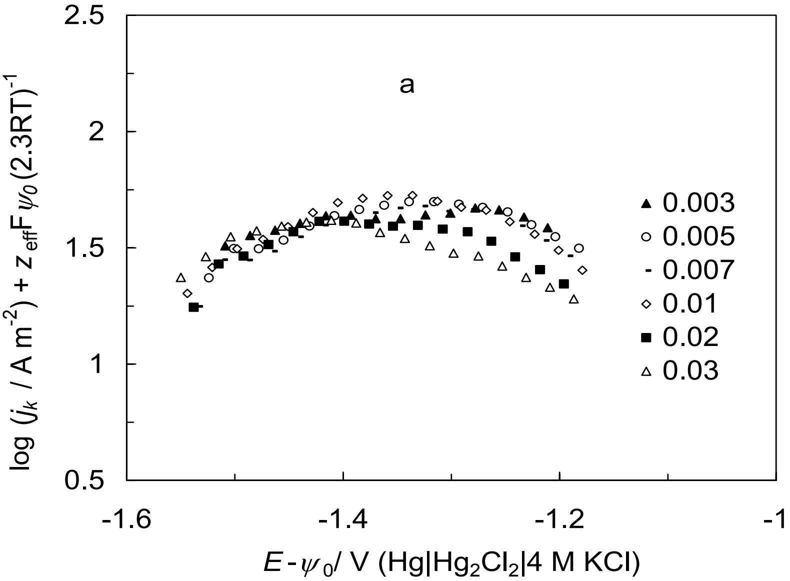
a
2.5
2
1.5
1
0.5
-1.6
-1.4
-1.2
-1
log (j_k / A m^{-2}) + $z_{eff}F\psi_0(2.3RT)^{-1}$
$E - \psi_0$/ V (Hg|Hg$_2$Cl$_2$|4 M KCl)
▲ 0.003
○ 0.005
- 0.007
◇ 0.01
■ 0.02
△ 0.03

Fig. 9a

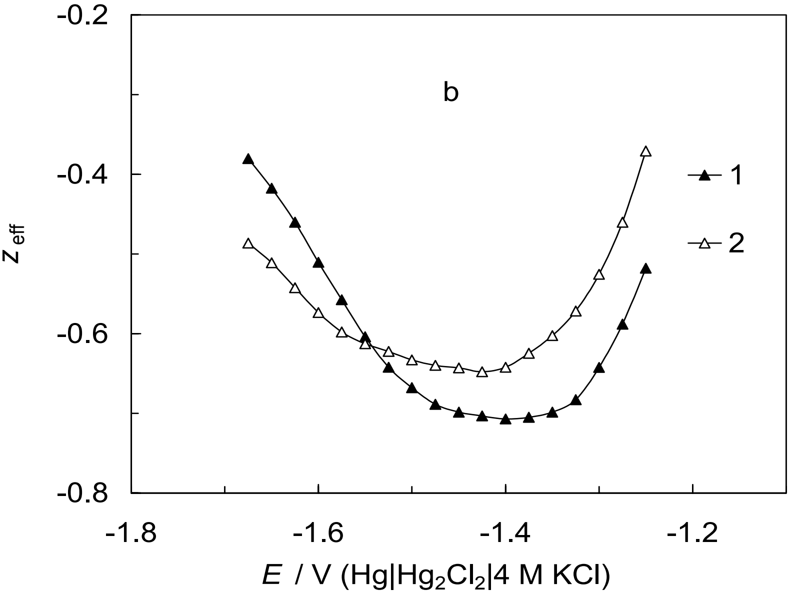
b
-0.2
-0.4
-0.6
-0.8
-1.8
-1.6
-1.4
-1.2
z_{eff}
E / V (Hg|Hg$_2$Cl$_2$|4 M KCl)
1
2

Fig. 9b

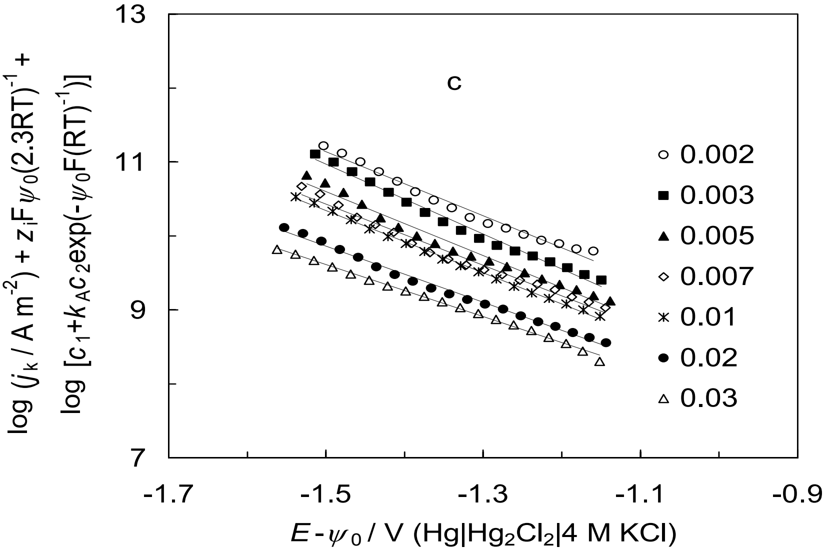

Fig. 9c

Fig. 9. Corrected Tafel plots at $z_i = z_{eff}$ for the EP Cd(0001) plane in 4×10^{-5} M $Na_2S_2O_8$ solutions with different additions of Na_2SO_4 (M), noted in figure (a). Effective charge vs. electrode potential dependences (calculated using the Frumkin-Petrii method) for the EP Cd(0001) plane (b): in 4×10^{-5} M $Na_2S_2O_8$ solutions with additions of 0.005 M NaF (1) and 0.005 M Na_2SO_4 (2). Corrected Tafel plots calculated according to Eq. (8) ($z_i = -2$ and $\psi_1 = \psi_0$) for the EP Cd(0001) plane in 4×10^{-5} M $Na_2S_2O_8$ solutions with different additions of Na_2SO_4 (M), noted in figure (c).

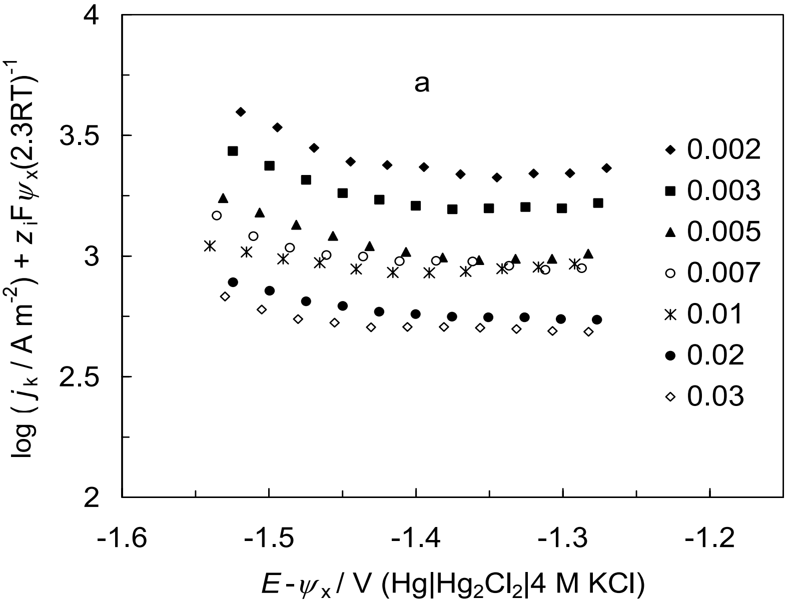

Fig. 10a

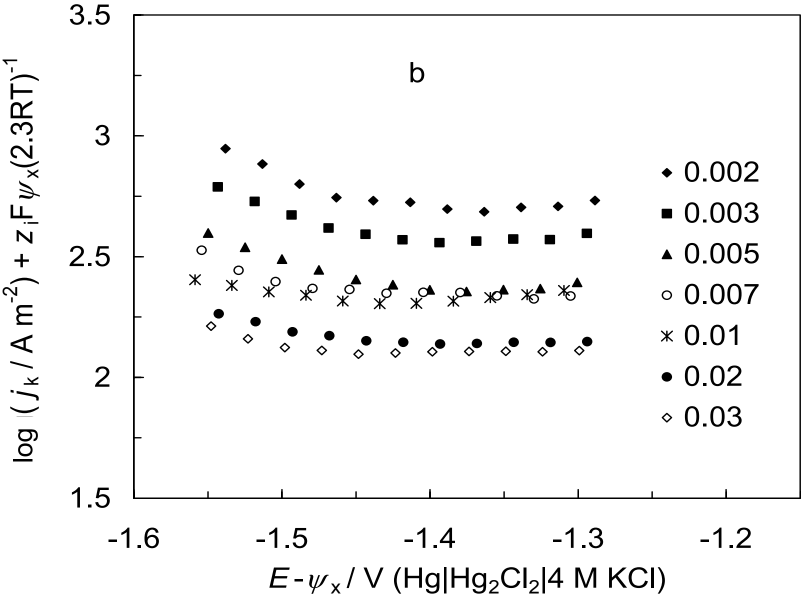

Fig. 10b

Fig. 10. Corrected Tafel plots calculated according to Eq. (3) ($z_i = -2$ and $\psi_1 = \psi_x$) for the EP Cd(0001) plane in 4×10^{-5} M $Na_2S_2O_8$ solutions with different additions of NaF (M, noted in figure) at the fixed distance: (a) $x = 0.2$ nm and (b) $x = 0.43$ nm of the reaction site from the outer Helmholz plane.

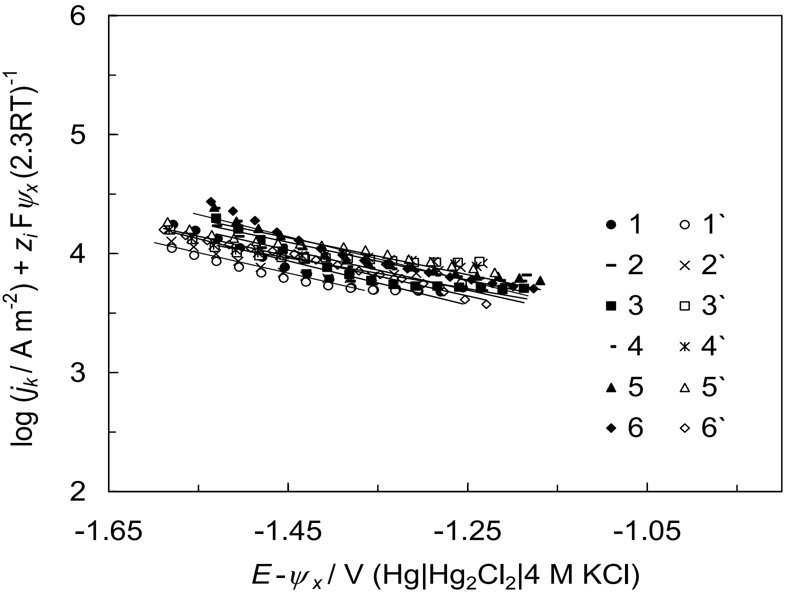

Fig. 11. Corrected Tafel plots (calculated according to Eq. (3) if $z_i = -2$ and $\psi_1 = \psi_x$) for the EP Cd(0001) plane in 4×10^{-5} M $Na_2S_2O_8$ solutions with different additions of Na_2SO_4 (1–6) and NaF (1'–6') (M): 1,1' — 0.002; 2,2' — 0.003; 3,3' — 0.005; 4,4' — 0.007; 5,5' — 0.01; and 6,6' — 0.02, assuming that $x = f(c_f)$ and the term $[-\kappa x]$ = const. in Eq. (3).

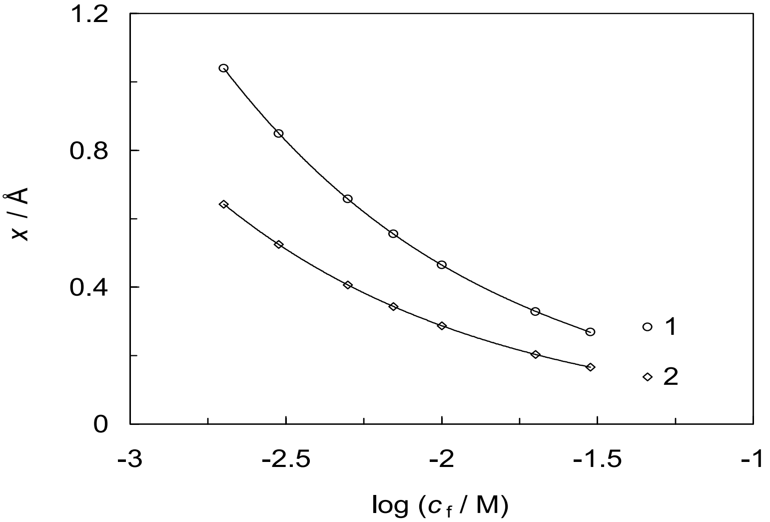

Fig. 12. The dependences of the effective distance of the reaction site from the outer Helmholtz plane on the base electrolyte concentration for EP Cd(0001) in the NaF (1) and Na_2SO_4 (2) solutions, calculated using Eq. (3) and data in Fig. 11.

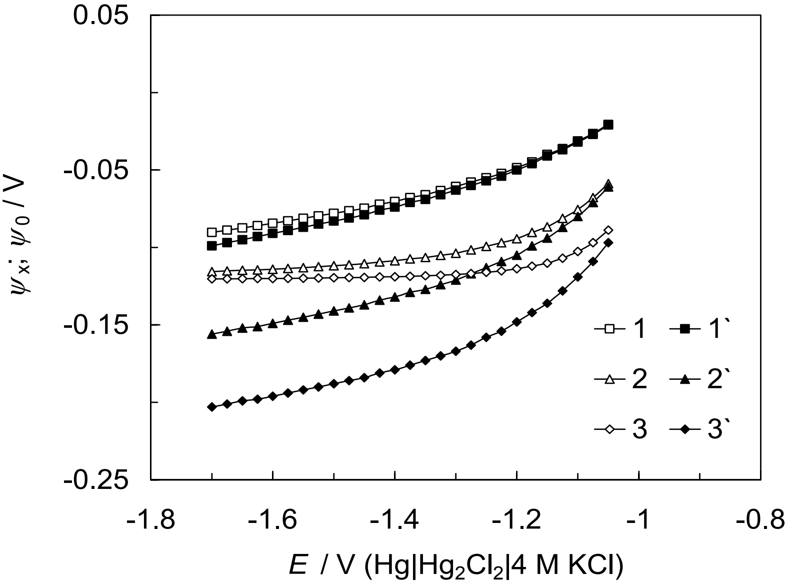

Fig. 13. Classical Gouy – Chapman ψ_0 potential (1’–3’) and effective ψ_x potential (1–3) (used for the calculation of cTps in Fig. 10) vs. electrode potential dependences for Cd(0001) electrode at the conditions $x = f(c_{\mathrm{Na_2SO_4}})$ and the term $[-\kappa x]$ = const. in Eq. (3) in Na_2SO_4 solutions (M): 1,1’ – 0.1; 2,2’ – 0.01; 3,3’ – 0.002.

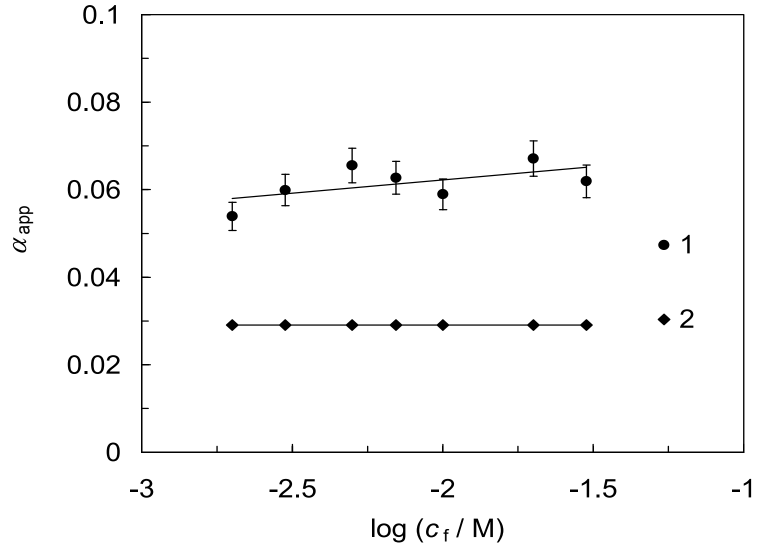

Fig. 14. The apparent transfer coefficient α_{app} vs. c_{f} dependences for EP Cd(0001) for NaF (1) and Na_2SO_4 (2), assuming that $x = f(c_{\mathrm{f}})$ and the term $[-\kappa x]$ = const. in Eq. (3).

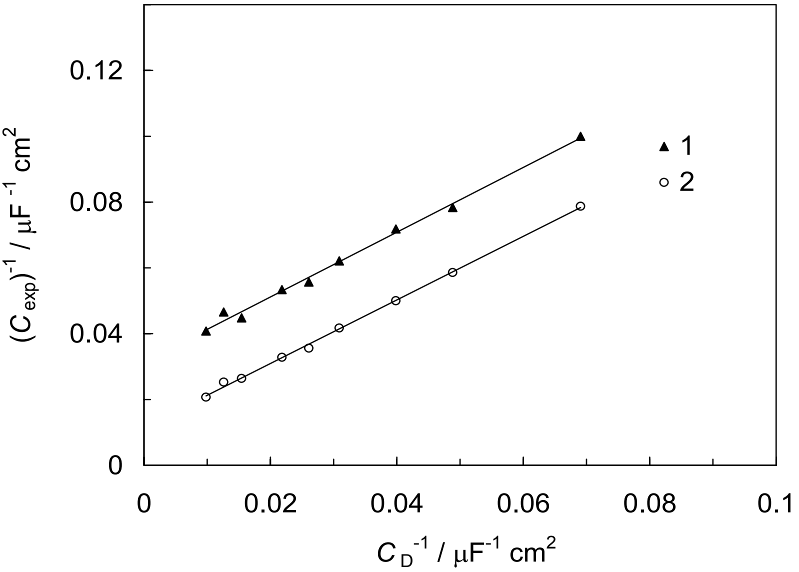

Fig. 15. Dependences of the inverse experimental differential capacitance on the calculated inverse diffuse layer capacitance according to the Gouy-Chapman (1) and Gonzalez-Sanz (2) models for the Cd(0001) electrode in the base electrolyte (Na_2SO_4) solution.

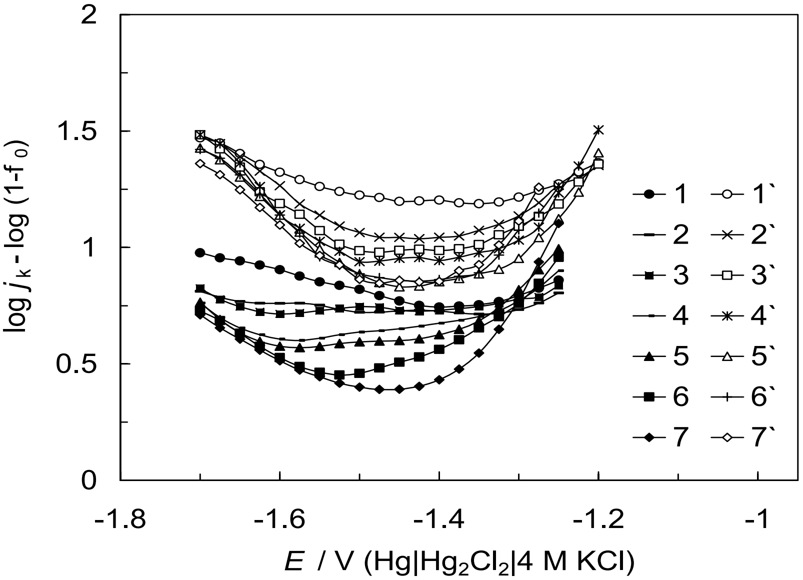

Fig. 16. The logj_k – log(1–f_0) dependences (calculated according to Gonzalez-Sanz [34] and Damaskin et al. [30] models) for EP Cd(0001) in 4×10^{-5} M $Na_2S_2O_8$ solutions with addition of NaF (1–6) and Na_2SO_4 (1'–6') (M): 1;1' – 0.03; 2;2' – 0.02; 3;3' – 0.01; 4;4' – 0.007; 5;5' – 0.005; 6;6' – 0.003; and 7;7' – 0.002.

8. CONCLUSIONS

The influence of the base electrolyte nature, concentration and electrode polarisation on the electroreduction of the peroxodisulfate anion at the EP Cd(0001) plane has been studied by linear sweep and rotating disc electrode voltammetry methods. The rate constant of the heterogeneous electroreduction reaction of the $S_2O_8^{2-}$ anion on the electrochemically polished EP Cd(0001) plane depend on the base electrolyte concentration and electrode polarisation has been established. In the region of zero charge potential the electroreduction of the $S_2O_8^{2-}$ anions is limited by the rate of diffusion of $S_2O_8^{2-}$ anions and in the region of small negative surface charge densities the inhibition of $S_2O_8^{2-}$ anion electroreduction takes place. At very negatively charged Cd(0001) surface the exchange of the electroreduction mechanism of $S_2O_8^{2-}$ anions is possible, i.e. additionally to the usual charge transfer process the simultaneous charge transfer through the adsorbed ion-pairs is probable.

The values of apparent transfer coefficient a_{app}, corrected for the double layer effect, noticeably lower than 0.5 for the EP Cd(0001) plane have been obtained, only very weakly depending on the electrode potential and electrolyte concentration. The different models for the calculation of the diffuse layer potential correction of the kinetic current density have been used to construct the so-called corrected Tafel plots. The coincidence of the corrected Tafel plots for the solutions with different base electrolyte concentrations has been established if the effective distance of the reaction site from the outer Helmholtz plane is assumed to be inversely proportional to the base electrolyte concentration in the solution. The very low values of the apparent charge transfer coefficient show that the activationless charge transfer mechanism is probably valid for EP Cd(0001) | base electrolyte + $Na_2S_2O_8$ aqueous solution interface in a good agreement with the theoretical models for the high hydrogen overvoltage metals based on the diabatic charge transfer mechanism from the metal to an ion.

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10. SUMMARY IN ESTONIAN

Käesolevas töös uuriti peroksodisulfaatanioonide elektrokeemilist redutseerumist elektrokeemiliselt poleeritud Cd(0001) monokristalli tahul kasutades selleks tsüklilist voltamperomeetriat, mis oli kombineeritud pöörleva ketaselektroodi seadmega. Leiti, et peroksodisulfaataniooni redutseerumise kiirus sõltub nii foonelektrolüüdi iseloomust, kontsentratsioonist kui ka elektroodi potentsiaalist. Null-laengupotentsiaali alas on reaktsiooni limiteerivaks staadiumiks difusioon. Elektroodi negatiivsemate pinnalaengute korral toimub reaktsiooni kiiruse vähenemine, mis on tingitud negatiivselt laetud peroksodisulfaatanioonide tõukumisest Cd(0001) elektroodi pinnalt. Veelgi negatiivsematel pinnalaengutel võib aga toimuda reaktsioonimehhanismi muutus, kus lisaks otsesele laenguülekandel mehhanismile võib paralleelselt toimuda ka laenguülekanne läbi pinnale adsorbeerunud ioonpaaride.

Kasutades erinevaid lähendusmudeleid, konstrueeriti nn parandatud Tafeli sõltuvused, mille tõusust on võimalik määrata laenguülekande koefitsiendi a_{app} väärtusi. Parandatud Tafeli-sõltuvuste kõige parem kokkulangevus saavutati eeldusel, et reaktsiooni astuva osakese kaugus välisest Helmholtzi tasandist on pöördvõrdelises seoses foonelektrolüüdi kontsentratsiooniga. Tehti kindlaks, et määratud näilise laenguülekande koefitsiendi väärtused on praktiliselt sõltumatud foonelektrolüüdi kontsentratsioonist ja väga madalad a_{app} väärtused näitavad, et tõenäoliselt on tegemist aktivatsioonienergiata laenguülekande mehhanismiga.

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12. PUBLICATIONS

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