

The kinetics of electroreduction of europium(III) cations at bismuth single-crystal electrode

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Abstract Electroreduction of $\text{Eu}(\text{ClO}_4)_3$ and $\text{Eu}_2(\text{SO}_4)_3$ has been studied at electrochemically polished $\text{Bi}(01\bar{1})$ single-crystal electrode in an acidic HClO_4 or H_2SO_4 (pH ~3) aqueous solution with LiClO_4 or Na_2SO_4 additions as a surface inactive electrolyte. The Eu^{3+} cations electroreduction rate depends on the electrode potential applied and the concentration of the supporting electrolyte as well as the concentration of the Eu^{3+} ions. At the more negative electrode potentials than the zero charge potential (zcp), the diffusion current plateaus were observed. The values of the rate constant for the heterogeneous reaction calculated at zcp are independent of the base electrolyte concentration studied. Analysis of the kinetic data corrected for the electrical double-layer effect shows that the coincidence of the corrected Tafel plots can be achieved, assuming that the effective charge of a reactant (+1.6) is significantly lower than it would be expected ($z_A=+3$).

Keywords Electroreduction · Europium(III) cation · Bismuth single crystal · Rate constant of heterogeneous reaction · Double-layer effects

Introduction

During recent years, there has been a considerable interest in fundamental studies of electron-transfer kinetics at solid electrodes and well-defined single-crystal planes [1–23], however systematic data are available only for some redox couples at single crystals [7, 24–29]. It is evident from the

literature data that studies of the electrical double-layer (edl) effects on the electron-transfer kinetics at single-crystal electrodes are important in assessing the role of the metal electronic properties on the electron-transfer kinetics [2, 3, 7, 24–29]. Electroreduction kinetics of Eu^{3+} at boron-doped diamond [30], Hg drop, gallium, lead as well as at thallium electrodes has been studied by many authors [31–36]. Weaver and Anson studied the one-electron reduction of Eu^{3+} in acidified NaClO_4 , LiClO_4 , $\text{La}(\text{ClO}_4)_3$, and also in mixed supporting electrolytes [33–35]. Fawcett et al. examined the same reaction on the mercury drop electrode in an acidic 10^{-3} M HClO_4 solution with variable NaClO_4 additions (0.3 and 0.03 M) [32, 36].

The main aim of this work was to investigate the electroreduction of $\text{Eu}(\text{ClO}_4)_3$ and $\text{Eu}_2(\text{SO}_4)_3$ at electrochemically polished $\text{Bi}(01\bar{1})$ single-crystal plane electrode in an acidic HClO_4 or H_2SO_4 aqueous solution with x M LiClO_4 or x' M Na_2SO_4 additions, respectively, and to compare the data with previous data for Hg and other electrodes [31–36] and with our previous results for electroreduction kinetics of $[\text{Co}(\text{NH}_3)_6]^{3+}$ cations at $\text{Bi}(hkl)$ electrodes [25–27].

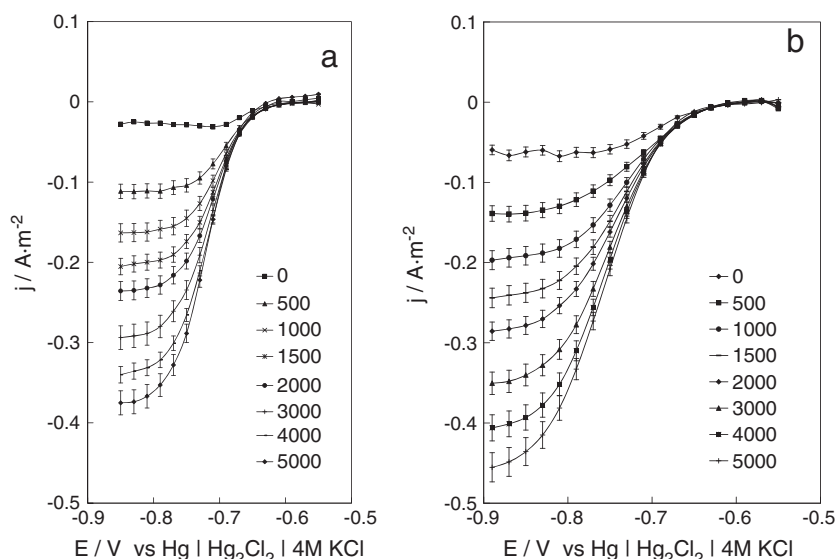
In the case of europium(III) solutions, it was important to maintain solution pH at 3 to prevent hydrolysis of the europium (III) cations [32, 37, 38] because the reduction rates of Eu^{3+} cations are independent of pH only at ≤ 3 . It should be remembered that the electroreduction reactions of ions have extremely strong influence on the structure of edl and potential distribution near the electrode surface [34, 39, 40].

Experimental

Conventional rotating disk electrode system from *Pine Instrument Company* was used for stationary and rotating disk voltammetry studies (potential scan rate of 10 mV s^{-1}

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Fig. 1 Rotating disk voltammetry curves (at potential scan rate of 10 mV s^{-1}) for Bi(01 $\bar{1}$) in $5 \times 10^{-5} \text{ M Eu}(\text{ClO}_4)_3 + 0.001 \text{ M HClO}_4 + 0.002 \text{ M LiClO}_4$ (a) and $2.5 \times 10^{-5} \text{ M Eu}_2(\text{SO}_4)_3 + 0.0005 \text{ M H}_2\text{SO}_4 + 0.001 \text{ M Na}_2\text{SO}_4$ (b) at various rotation velocities ν (rpm), noted in figure



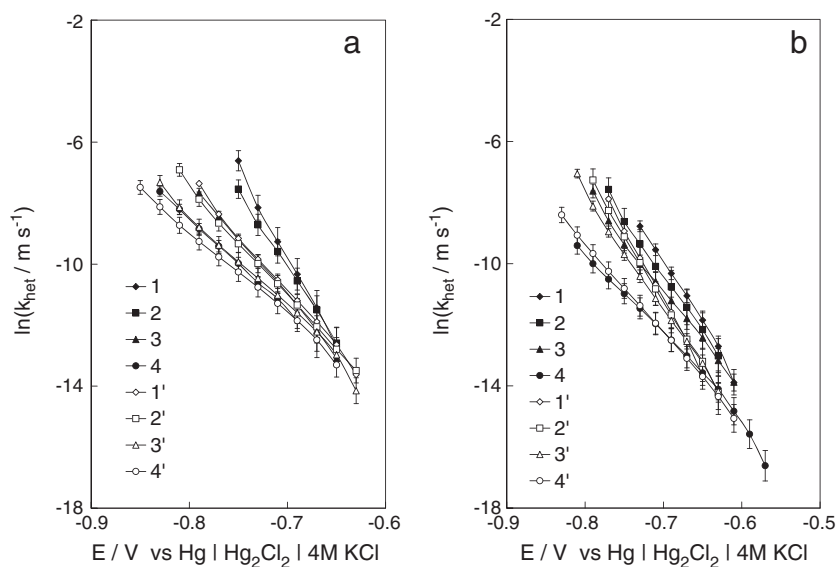
and rotation velocity from 0 to 5,000 rpm were used). Electrochemically polished Bi(01 $\bar{1}$) single-crystal plane electrode was used as a working electrode, which was prepared according to methods described in Refs. [25–29, 41]. The Bi(01 $\bar{1}$) electrode was selected for detailed study in view of the very good electrochemical stability (covalent bonds between the Bi atoms) and a wide region of ideal polarization [41]. The cleanliness of the base electrolyte solution and the quality of the electrode surface were verified by cyclic voltammetry and impedance spectroscopy methods as well as by in situ STM [28].

A conventional three-electrode glass cell was used for electrochemical studies. A calomel reference electrode filled with 4MKCl+H₂O solution and a large Pt counter

electrode were used. The reference electrode was connected to the cell through a long Luggin capillary. All kinetic data were measured within the range from -1.05 to $-0.55 \text{ V vs. Hg|Hg}_2\text{Cl}_2|4 \text{ M KCl}$ at temperature $T=298 \text{ K}$ under pure argon atmosphere (99.999%).

All solutions were prepared using MilliQ + water with resistivity $\geq 18.2 \text{ M}\Omega\text{cm}$. Glassware was cleaned with a hot H₂SO₄+H₂O₂ mixture and rinsed carefully with MilliQ + water before each set of measurements [32–34, 39, 40]. HClO₄, LiClO₄, H₂SO₄, Na₂SO₄, Eu₂(SO₄)₃, and Eu(ClO₄)₃ (all “Aldrich”) were of the best quality available. For accurate determination of a precision of the experimental data, a statistical treatment of the results was carried out. A total number of the independent experiments $m \geq 4$

Fig. 2 Logarithmic dependence of the experimental rate constant k_{het} on the electrode potential for Bi(01 $\bar{1}$) a in $5 \times 10^{-5} \text{ M Eu}(\text{ClO}_4)_3 + 0.001 \text{ M HClO}_4 + x \text{ M LiClO}_4$ (filled marks— x : 1, 0.001; 2, 0.002; 3, 0.01; and 4, 0.02) and in $2.5 \times 10^{-5} \text{ M Eu}_2(\text{SO}_4)_3 + 0.0005 \text{ M H}_2\text{SO}_4 + x' \text{ M Na}_2\text{SO}_4$ (open marks— x' : 1', 0.0005; 2', 0.001; 3', 0.005; and 4', 0.01) and b in $y \text{ M Eu}(\text{ClO}_4)_3 + 0.001 \text{ M HClO}_4 + 0.002 \text{ M LiClO}_4$ (filled marks— y : 1, 5×10^{-5} ; 2, 1×10^{-4} ; 3, 2×10^{-4} ; and 4, 1×10^{-3}) and in $y' \text{ M Eu}_2(\text{SO}_4)_3 + 0.0005 \text{ M H}_2\text{SO}_4 + 0.001 \text{ M Na}_2\text{SO}_4$ (open marks— y' : 1', 2.5×10^{-5} ; 2', 5×10^{-5} ; 3', 1×10^{-4} ; and 4', 5×10^{-4})



were used [32–34, 39]. The relative error in current density at the constant electrode potential E did not exceed 7%.

Results and discussion

Rotating disk electrode voltammetry data

A typical dependence of the reduction current density (j) on the electrode potential (E) for the reduction of $\text{Eu}(\text{ClO}_4)_3$ or $\text{Eu}_2(\text{SO}_4)_3$ in an acidic solution of LiClO_4 and Na_2SO_4 , respectively, is presented in Fig. 1. According to these data, the electroreduction current of the Eu^{3+} cation depends noticeably on the electrode potential and rotation velocity as well as somewhat on the base electrolyte composition (Fig. 1). The j, E curve, can be divided into three main areas. The electroreduction of Eu^{3+} is limited by the charge transfer step at $E \geq 0.65$ V. Within the region from -0.65 to -0.8 V the process is limited by the mixed kinetics (diffusion and charge transfer) and the current density increases with the increase of the rotating speed of an electrode. In the region of negative surface charge densities ($E \leq 0.8$ V), clearly visible current plateaus were observed (0–5,000 rpm). Hysteresis of current density between the negative and positive potential scan directions was not observed within all the region of

electrode potential measured. The experimental values of the diffusion coefficients are: $D = 4.2 \pm 0.4 \cdot 10^{-6} \text{cm}^2 \text{s}^{-1}$ in 0.002 M $\text{LiClO}_4 + 0.001$ M HClO_4 and $D = 5.7 \pm 0.5 \cdot 10^{-6} \text{cm}^2 \text{s}^{-1}$ in 0.0005 M $\text{H}_2\text{SO}_4 + 0.001$ M Na_2SO_4 aqueous solutions with addition of Eu^{3+} , were calculated respectively, which are in a good agreement with the values of D found from the literature ($D = 6.1 \cdot 10^{-6} \text{cm}^2 \text{s}^{-1}$ in 0.3 M $\text{NaClO}_4 + 0.001$ M HClO_4 and $D = 6.7 \cdot 10^{-6} \text{cm}^2 \text{s}^{-1}$ in 0.03 M $\text{NaClO}_4 + 0.001$ M HClO_4 [32]).

However, for more concentrated Eu^{3+} solutions ($c \geq 5 \cdot 10^{-4}$ M) the current density observed experimentally is lower than that expected. The current plateaus in j, E curve shift towards the more negative electrode potentials with increase of the Eu^{3+} concentration in solution.

Kinetic analysis

The kinetic parameters for the electroreduction reaction of the Eu^{3+} cation on the $\text{Bi}(01\bar{1})$ plane have been established and results have been compared with our previous results [25–29]. The kinetic current density j_k has been obtained from the linear Koutecky–Levich plots at constant potential

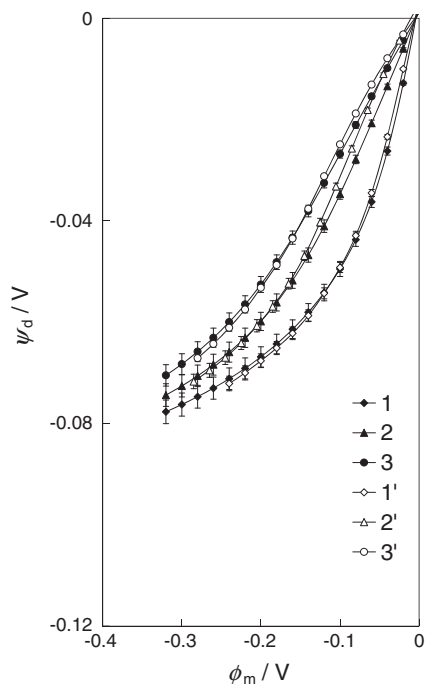


Fig. 3 Potential drop in the diffuse layer (ψ_d) vs. rotational electrode potential (ϕ_m) curves for $\text{Bi}(01\bar{1})$ in 5×10^{-5} M $\text{Eu}(\text{ClO}_4)_3 + 0.001$ M $\text{HClO}_4 + x$ M LiClO_4 (filled marks— x : 1, 0.001; 2, 0.01; and 3, 0.02) and in 2.5×10^{-5} M $\text{Eu}_2(\text{SO}_4)_3 + 0.0005$ M $\text{H}_2\text{SO}_4 + x$ M Na_2SO_4 (open marks— x' : 1', 0.0005, 2', 0.005, and 3', 0.01)

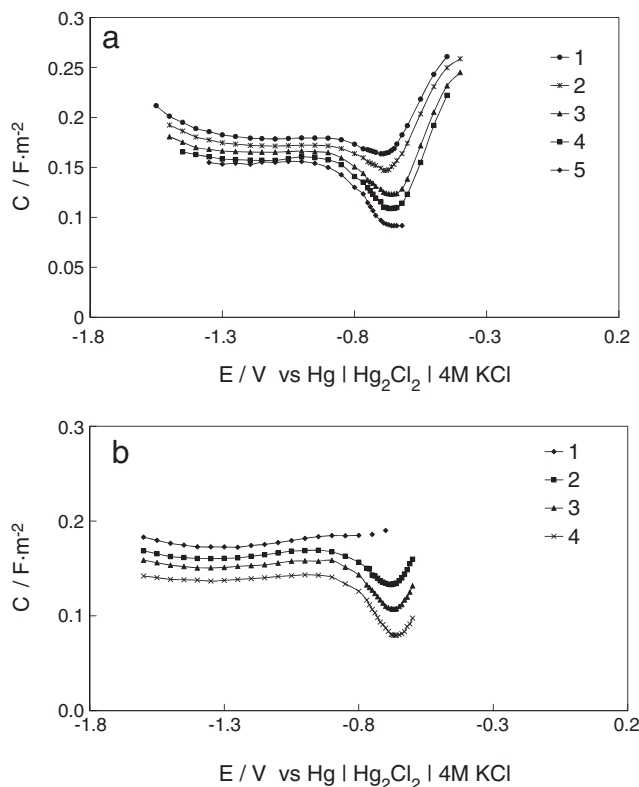


Fig. 4 Differential capacitance (at $\omega=0$) vs. electrode potential curves **a** for electrochemically polished $\text{Bi}(01\bar{1})$ electrode in LiClO_4 solution with concentrations (M): 1, 0.01; 2, 0.007; 3, 0.003; 4, 0.002; and 5, 0.001 and **b** for electrochemically polished $\text{Bi}(01\bar{1})$ electrode in Na_2SO_4 solution with concentrations: 1, 0.05; 2, 0.005; 3, 0.0025; and 4, 0.001

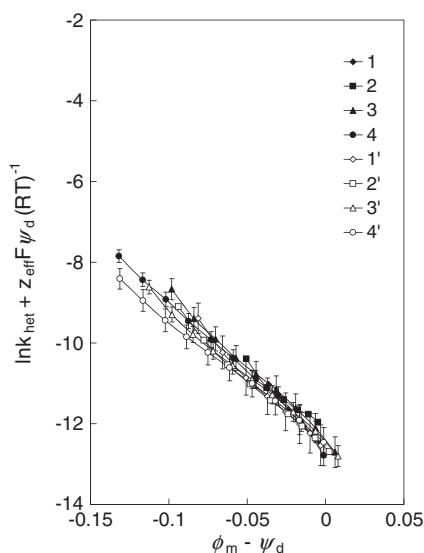


Fig. 5 Corrected Tafel plots calculated for Bi(011) in 5×10^{-5} M Eu(ClO_4)₃+0.001 M HClO₄+ x M LiClO₄ (filled marks— x : 1, 0.001; 2, 0.002; 3, 0.01; and 4, 0.02) and for 2.5×10^{-5} M Eu₂(SO₄)₃+0.0005 M H₂SO₄+ x 'M Na₂SO₄ (open marks— x ': 1', 0.0005; 2', 0.001; 3', 0.005; and 4', 0.01)

according to the ideas developed by Frumkin, Aikazyan and Tedoradze [42, 43]. The apparent rate constant for the electroreduction reaction of the Eu³⁺ cations, k_{het} , was defined as follows:

$$j_k = n_i F k_{\text{het}} c_i.$$

Figure 2 summarizes the kinetic data obtained for the reduction of the Eu(ClO_4)₃ and Eu₂(SO₄)₃ in the various supporting electrolytes and it shows that k_{het} values at electrode potentials near the zero charge potential ($E_{\sigma=0} = -0.65$ V in LiClO₄ and $E_{\sigma=0} = -0.67$ V in Na₂SO₄) obtained using the impedance spectroscopy method [41] are practically independent on the base electrolyte studied ($k_{\text{het}}^0 = 2.8 \cdot 10^{-3} (\pm 0.3)$ cm s⁻¹) (Fig. 2a). However k_{het} at $E < E_{\sigma=0}$ somewhat depends on the concentration of Eu³⁺ cation in solution (Fig. 2b) and similarly to [Co(NH₃)₆]³⁺ cations electroreduction reaction k_{het} weakly decreases with the rise of Eu³⁺ concentration. The values k_{het}^0 obtained at zero charge potential [44–49] are only weakly lower than that obtained for [Co(NH₃)₆]³⁺ electroreduction reaction on Bi(011) plane ($k_{\text{het}}^0 = 6.2 \cdot 10^{-3} (\pm 0.3)$ cm s⁻¹) [27]. However, the value $k_{\text{het}}^0 = 1.7 \cdot 10^{-4}$ cm s⁻¹ obtained for Hg electrode [50] in 1 M HClO₄ aqueous solution is weakly lower than that for Bi(011) plane. Somewhat lower standard rate constant value $k_{\text{het}}^0 = 1.2 \cdot 10^{-4}$ cm s⁻¹ has been calculated for Hg electrode in 1 mM NaF+Eu³⁺ aqueous solution [51]. It should be noted that more detailed comparison of data is complicated in case of Bi(011) it is impossible to use more concentrated HClO₄ solutions due to the lower hydrogen evolution overpotential compared with Hg [41–46].

The calculated values of experimental transfer coefficient for Bi(011) plane, α_{exp} , obtained from the data in Fig. 2 are noticeably higher than 0.5.

Kinetic data corrected for the electrical double-layer effect

At first, to calculate the so-called corrected Tafel plots (cTp), the absence of the specific adsorption of reactant and product was assumed, and thus the potential profile in the diffuse layer was calculated by the Gouy–Chapman theory [32, 44–46]. To construct a cTp, the experimental dependence of the rate constant k_{het} on the electrode potential is usually plotted as $(\ln k_{\text{het}} + z_A f \psi_d)$ against $(\phi_m - \psi_d)$, where z_A is the charge on the reacting species, $f = F/RT$ (where F is the Faraday constant, R is the universal gas constant, and T is the absolute temperature), and ϕ_m is rational potential of electrode ($\phi_m = E - E_{\sigma=0}$) [32].

The obtained ψ_d potential values, given in Fig. 3, were estimated using differential capacitance versus electrode potential data (given in Fig. 4), measured for a supporting base electrolyte, taking into account an asymmetry of the electrolyte systems studied. Assuming that $\psi_1 \approx \psi_d$ and charge $z_A = +3$ for the Eu³⁺ cation reduction, the cTp with different concentration of base electrolyte do not overlap, moreover the slopes of these plots are significantly different (ψ_1 is the potential of the plane at which the centers of the charges of the reacting particles are located in the transition state of a reaction and ψ_d is the potential at the outer Helmholtz plane [13, 42–46]). Then the charge z_A (so-called integer charge [49]) is assumed to be +2; the cTp are

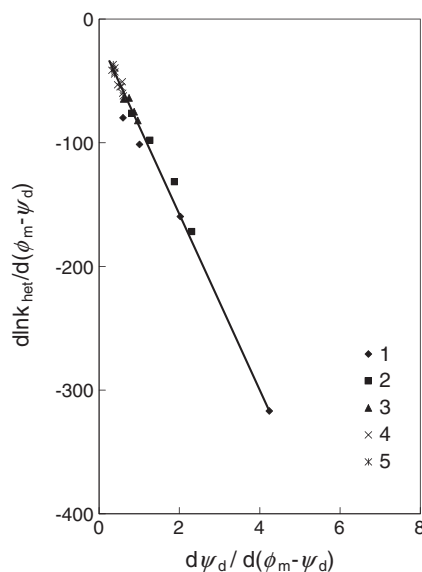


Fig. 6 $d \ln k_{\text{het}} / d(\phi_m - \psi_d)$ vs. $d \psi_d / d(\phi_m - \psi_d)$ dependences for electrochemically polished Bi(011) in 5×10^{-5} M Eu(ClO_4)₃+0.001 M HClO₄+ x M LiClO₄ aqueous solutions— x : 1, 0.001; 2, 0.002; 3, 0.003; 4, 0.01; and 5, 0.02

closer to each other but still do not overlap well enough for systems studied. It should be noted that the similar results have been achieved using the quantum chemical calculations by Fawcett et. al. [32].

Analysis of the experimental cTp shows (Fig. 5) that if the so-called effective charge values were calculated from the slope of $d(\ln k_{\text{het}})/d(\phi_m - \psi_d)$ against $d\psi_d/(\phi_m - \psi_d)$ plots (Fig. 6) according to Fawcett and Henderson models [32, 47, 48], there is a good overlapping of cTp data independent of the base electrolyte chemical composition and concentration applied. The effective charge value $z_{\text{eff}}=+1.6$ obtained for Eu^{3+} cations electroreduction reaction in the acidified dilute $\text{LiClO}_4+\text{HClO}_4$ electrolyte solution is in a good agreement with the experimental data reported by Fawcett et. al [32]. The noticeable lower effective charge values $z_{\text{eff}}=+0.52$ were calculated for $[\text{Co}(\text{NH}_3)_6]^{3+}$ cations containing solutions [26, 27]. The transfer coefficient values only slightly higher from 0.5 were calculated from the cTp using effective charge value $z_{\text{eff}}=+1.6$ for Eu^{3+} electroreduction reaction at $\text{Bi}(01\bar{1})$ plane.

Conclusions

The electroreduction kinetics of the europium(III) cations on the electrochemically polished $\text{Bi}(01\bar{1})$ single-crystal plane has been studied by rotating disk electrode and impedance spectroscopy methods. It was found that at the electrode potentials $E \leq 0.8$ V versus $\text{Hg}|\text{Hg}_2\text{Cl}_2|4\text{MKCl}$, the electroreduction of Eu^{3+} cations is limited mainly by the rate of the diffusion step and the calculated diffusion coefficients are in a good agreement with literature data [27]. The apparent rate constant for the electroreduction of the Eu^{3+} cations at $E < E_{\sigma=0}$, k_{het} , decreases with the increase of concentrations of the supporting electrolyte as well as Eu^{3+} ions concentration in solution. At zero charge potential $E_{\sigma=0}$, the value of k_{het}^0 can be obtained experimentally, independent of base electrolyte addition studied. It should be noted that the construction of the dependence of rate constant corrected for electrical double-layer effect, on the diffuse layer potential drop (i.e., $d(\ln k_{\text{het}})/d(\phi_m - \psi_d)$ against $d\psi_d/(\phi_m - \psi_d)$ plots) gives a lower effective charge value ($z_{\text{eff}}=+1.6$) for reacting complex of the europium(III) cation, surrounded with the solvent molecules and surface inactive electrolyte ions, than expected. Probably the effective charge for the reacting species is affected by the surrounding electrolyte, i.e., anions in solution (SO_4^{2-} and ClO_4^-). This can be explained by the big ionic radius of the europium(III) cation obtaining comparatively low hydration energy for Eu^{3+} cations and thus ability to form ionic associates, as well as by the weak dependence of the closest approach of ions to the electrode surface, i.e., by the small differences in the electrical double-layer structure in the systems studied.

It was found that an analysis of kinetic data for reactants with an asymmetrical distribution of the charge may play significant role in the constructing of cTp. However, on the basis of experimental data, it is clear that these multivalent redox systems are quite complex.

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